The *Proceedings of the National Academy of Sciences, India,* is published in two sections: Section—A (Physical Sciences) and Section—B (Biological Sciences). Six parts of each section are published annually.

The Editorial Board in its work of examining papers received for publication is assisted, in an honorary capacity, by a large number of distinguished scientists. Papers are accepted from members of the Academy *in good standing.* In case of a joint paper, one of the authors must be a member of the Academy. The Academy assumes no responsibility for the statements and opinions advanced by the authors. The papers must conform strictly to the rules for publication of papers in the *Proceedings.* A total of 50 reprints are supplied free of cost to the author or authors. The authors may have any reasonable number of additional reprints at cost price, provided they give prior intimation while returning the proof.

Communications regarding contributions for publication in the *Proceedings,* books for review, subscriptions, etc., should be sent to the General Secretary, The National Academy of Sciences, India, Lajpatrai Road, Allahabad-2 (India).

Annual Subscription for each Section: Rs. 30 (Inland); 60 sh. (Foreign)
Single Copy: Rs. 5 (Inland); 10 sh. (Foreign).

SOME ASYMPTOTIC PROBLEMS OF SOLUTIONS OF DIFFERENTIAL SYSTEMS

BY V. LAKSHMIKANTH

(*Department of Mathematics, Osmania University, Hyderabad-Deccan-7*)

INTRODUCTION

THE aim of the paper is to consider some asymptotic problems of solutions of differential systems in a more general way. It is divided into three sections. The first section deals with the problems of the solutions of differential systems. We consider in the second section problems of solutions of perturbed differential systems and unperturbed differential systems. In the last section, we apply our results to second order differential equations.

(i) Consider the differential system

$$y_i' = f_i(t, y_1, \ldots . y_n); \quad y(t_o) = c_i \tag{1}$$

where f_i are continuous in the region $0 \leqslant t < \infty$; $|y_i| < \infty$. The boundedness of any solution of the equations (1) has been investigated by A. Wintner,[1] B. Viswanatham[2] and V. Lakshmikanth.[3] The type of problem that will be considered in this section is this:

If $y_i(t)$ is any solution of the equations (1), what are the assumptions that guarantee the existence of an order relation

$$|y_i'(t)| + |y_i(t)| = 0 [k_i(t)] \quad \text{as} \quad t \to \infty \tag{2}$$

where $k_i(t) > 0$ are continuous functions in the domain $0 \leqslant t < \infty$.

We shall say that the functions $h_i(t, r_1, r_2, \ldots . r_n)$ have the property (*) if the functions $h_i \geqslant 0$ are continuous and bounded in the region $0 \leqslant t < \infty$; $r_i > 0$;

non-decreasing in r_i. This implies that there is a "maximum" solution $m_i(t)$ such that $m_i(t) \geqslant n_i(t)$ for every other solution $n_i(t)$: cf. Kamke.[4] In the sequel, we use the symbol exclusively to denote this maximum solution of

$$r_i' = h_i(t, r_1, \ldots \ldots r_n); \quad r_i(t_0) = c_i. \tag{3}$$

In the course of our discussion, we shall use the following:

PRELIMINARY THEOREM 1. Let (i) the functions $h_i(t, r_1, \ldots r_n)$ have the property (*);

(ii) the functions $r_i(t)$ be continuous in the region $0 \leqslant t < \infty$ and satisfy

$$r_i(t_0) = c_i; \quad r_i(t) \leqslant c_i + \int_{t_0}^{t} h_i\{s, r_1(s), \ldots \ldots r_n(s)\}\, ds \tag{4}$$

then

$$r_i(t) \leqslant m_i(t) \quad \text{for} \quad t_0 \leqslant t < \infty.$$

Proof.—Let us take $z_i^{(1)}(t) = r_i(t)$ as a first approximation to the solution of differential system (3). Then

$$z_i^{(2)}(t) = c_i + \int_{t_0}^{t} h_i\{s, z_1^{(1)}(s), \ldots \ldots z_n^{(1)}(s)\}\, ds$$

is a second approximation and so on. Our condition (4) just states $z_i^{(2)}(t) \geqslant z_i^{(1)}(t)$. Now

$$z_i^{(3)}(t) - z_i^{(2)}(t) = \int_{t_0}^{t} [h_i\{s, z_1^{(2)}(s), \ldots \ldots z_n^{(2)}(s)\} - h_i\{s, z_1^{(1)}(s), \ldots \ldots \\ z_n^{(1)}(s)\}]\, ds \geqslant 0$$

since the functions h_i are non-decreasing in r_i. It follows from the above that $z_i^{(3)}(t) \geqslant z_i^{(2)}(t)$. Hence by induction we obtain $z_i^{(k+1)}(t) \geqslant z_i^{(k)}(t)$.

It is clear from the above inequalities that the successive approximations $z_i^{(k)}(t)$ is monotonic sequence of functions uniformly bounded and equicontinuous for each fixed i and therefore converge uniformly to a solution of the differential system (3), say $z_i(t)$. It then follows $r_i(t) \leqslant z_i(t)$. But $z_i(t) \leqslant m_i(t)$ where $m_i(t)$ is the maximum solution of the system (3). Hence

$$r_i(t) \leqslant m_i(t) \quad \text{for} \quad t_0 \leqslant t > \infty.$$

This is an extension to system of a result proved in [2].

Now, we are in a position to prove the following:

THEOREM 2. Let (i) the functions $h_i(t, r_1, \ldots r_n)$ have the property (*);

(ii) the maximum solution $m_i(t)$ satisfy the order relation

$$m_i(t) + m_i'(t) = 0\{k_i(t)\} \quad \text{as} \quad t \to \infty \tag{5}$$

where $k_i(t) > 0$ are continuous functions in the region $t_0 \leqslant t < \infty$;

(iii) the functions f_i of the differential system (1) satisfy the conditions

$$|f_i(t, y_1, \ldots y_n)| \leqslant h_i(t, |y_1|, \ldots |y_n|); \tag{6}$$

then every solution $y_i(t)$ of the differential system (1) has the property

$$|y_i(t)| + |y_i'(t)| = 0\,[k_i(t)] \quad \text{as} \quad t \to \infty.$$

Proof.—Any solution $y_i(t)$ of the system (1) is given by

$$y_i(t) = c_i + \int_{t_0}^{t} f_i\{s, y_1(s), \ldots y_n(s)\}\,ds \tag{7}$$

It then follows that

$$|y_i(t)| \leqslant |c_i| + \int_{t_0}^{t} |f_i\{s, y_1(s), \ldots y_n(s)\}\,ds.$$

We obtain from the condition (6)

$$|y_i(t)| \leqslant |c_i| + \int_{t_0}^{t} h_i\{s, |y_1(s)|, \ldots |y_n(s)|\}\,ds.$$

An appeal to Theorem 1 yields

$$|y_i(t)| \leqslant m_i(t) \quad \text{for} \quad t_0 \leqslant t > \infty. \tag{8}$$

The equations (7) imply

$$y_i'(t) = f_i\{t, y_1(t), \ldots y_n(t)\}$$

together with the condition (6) this gives

$$|y_i'(t)| \leqslant h_i\{t, |y_1(t)|, \ldots |y_n(t)|\}$$

since the functions h_i are monotonic non-decreasing in r_i, we obtain using the inequalities (8)

$$|y_i'(t)| \leqslant h_i\{t, m_1(t), \ldots m_n(t)\} = m_i'(t) \text{ for } t_0 \leqslant t < \infty. \tag{9}$$

he inequalities (8) and (9) together with the assumption (5) gives the required esult:

$$|y_i(t)| + |y_i'(t)| = 0\,\{k_i(t)\} \quad \text{as} \quad t \to \infty.$$

The special case

$$h_i(t, r_1, \ldots r_n) = L_i(t)\, r_i \tag{10}$$

where $L_i(t)$ is non-negative and continuous in the region $0 \leqslant t < \infty$ [and for

which case $m_i(t) = c_i \exp. \int_{t_0}^{t} L_i(s)\,ds$] gives the following theorem which has

been recently investigated by A. Wintner.[5]

THEOREM 3. Let (i) the functions $L_i(t) \geqslant 0$ be continuous in the region $0 \leqslant t < \infty$ and satisfy the order relation

$$\{1 + L_i(t)\} \exp. p_i(t) = 0 \{k_i(t)\} \quad \text{as} \quad t \to \infty \tag{11}$$

where $p_i(t)$ are defined by

$$p_i(t) = \int_{t_0}^{t} L_i(s)\, ds; \tag{12}$$

(ii) the functions f_i of the differential system (1) satisfy the condition

$$|f_i(t, y_1, \ldots y_n)| \leqslant L_i(t) |y_i|$$

then every solution $y_i(t)$ of the system (1) satisfies the relation (2).

The following is a more general:

THEOREM 4. Let (i) the functions $h_i(t, r_1, r_2, \ldots r_n)$ have the property (*);

(ii) the maximum solution $m_i(t)$ satisfy the order relation (5);

(iii) the functions f_i of the differential system (1) satisfy the condition

$$|f_i(t, y_1, \ldots y_n) \pm f_i(t, y_1^*, \ldots y_n^*)|$$
$$\leqslant h_i(t, |y_1 \pm y_1^*|, \ldots, |y_n \pm y_n^*|);$$

Then the sum or the difference $d_i(t)$ of any two solutions of the system (1) has the property

$$|d_i(t)| + |d_i'(t)| = 0 [k_i(t)] \quad \text{as} \quad t \to \infty$$

where $k_i(t) > 0$ are continuous in the region $0 \leqslant t < \infty$.

Corollary: If in addition we have $f_i(t, 0, \ldots 0) = 0$, the result of Theorem 2 follows from that of Theorem 4.

Next we shall state a comparison theorem. Consider the differential system

$$x_i' = g_i(t, x_1, x_2, \ldots x_n); \quad x_i(t_0) = c_i \tag{14}$$

where the functions g_i are continuous in the domain $0 \leqslant t < \infty$, $|x_i| < \infty$.

THEOREM 5. Let (i) the functions $h_i(t, r_1, \ldots r_n)$ have the property (*);

(ii) the maximum solution $m_i(t)$ satisfy the order relation (5);

(iii) the functions f_i and g_i of the differential systems (1) and (14) respectively satisfy the condition

$$|f_i(t, y_1, \ldots y_n) \pm g_i(t, x_1, \ldots x_n)|$$
$$\leqslant h_i(t, |y_1 \pm x_1|, \ldots, |y_n \pm x_n|);$$

then the sum or the difference $d_i(t)$ of any two solutions of the systems (1) and (14) satisfies the order relation

$$|d_i(t)| + |d_i'(t)| = 0 \{k_i(t)\} \quad \text{as} \quad t \to \infty$$

where $k_i(t)$ have usual meaning.

Corollary: If in addition, we have $f_i (t, 0, \ldots 0) \equiv 0$, then every solution of the system (14) satisfies an order relation of the type (2).

The proofs of the above theorem are similar to that of the Theorem 2 and hence omitted.   ✿

PERTURBED DIFFERENTIAL SYSTEMS

In this section we shall consider the asymptotic problems of solutions of perturbed differential systems.

Consider the following differential system written in the vectorial form

$$y' = A(t)y + f(t, y) \tag{15}$$

where $A(t) = \| a_{ij}(t) \|$ is a $n \times n$ matrix and y and f are column vectors of n components each. Define

$$\| A(t) \| = \sum_{i,j=1}^{M} | a_{ij}(t) |;$$

and

$$| A_i(t) | = \sum_{j=1}^{M} | a_{ij}(t) |.$$

We assume that $a_{ij}(t)$ and $f_i(t, y_1, \ldots y_n)$ are continuous functions in the region $0 \leqslant t < \infty$ and $| y_i | < \infty$.

Let the unperturbed system be

$$y' = A(t)y. \tag{16}$$

The following results will be established for convenience.

Lemma 1.—Equation (16) has n linearly independent vector solutions.

Proof.—To prove this, let a_i, $i = 1, 2, \ldots n$, be linearly independent points in the n-dimentional y space. For example, each a_i may be taken as a vector with all components zero except the i-th, which is 1. Then, by existence theorem, there exist n solutions y_i, $i = 1, 2, \ldots n$, of (16) such that $y_i(0) = a_i$. Now suppose on the contrary, that y_i are linearly dependent. Then there must exist n real numbers k_i such that $\sum k_i y_i(t) = 0$. This implies that $\sum k_i y_i(0) = \sum k_i a_i = 0$ and this contradicts the assumption that the a_i are linearly independent. This proves that the y_i are linearly independent.: *cf.* [9]

Let Y be the $n \times n$ matrix whose columns are the n vector solutions y_i, y_i being so chosen to satisfy the initial conditions Y (0) = unit matrix. Since each column of Y is a solution of (16) it is clear that Y satisfies

$$y' = A(t)Y; \quad Y(0) = \text{unit matrix.} \tag{17}$$

Lemma 2.—Y (t) is non-singular in the interval $0 \leqslant t \leqslant t_0 < \infty$. More precisely

$$| Y | = \exp \left\{ \int_0^t \sum a_{ii}(s) \, ds \right\}.$$

Proof.—The proof depends upon the following two facts:

(i) $d \mid Y \mid /dt =$ sum of the determinants formed by replacing the elements of one row of $\mid Y \mid$ by their derivatives

(ii) the columns of Y are solutions of the vector equation

$$y' = A(t) y.$$

simplifying the determinants obtained in (i) by use of (ii), we obtain

$$d \mid Y \mid /dt = \{ \Sigma \ a_{ii}(t) \} \mid Y \mid$$

since $\mid Y(0) \mid = 1$, the result follows: *cf.* [10]

Lemma 3.—If (i) $r(t)$ be a solution of (15), $r(0) = c$; (ii) $Y(t)$ be the matrix solution of (17), then $r(t)$ satisfies the integral equation

$$r(t) = Y(t) c + \int_0^t Y(t) Y^{-1}(s) f\{s, r(s)\} ds. \qquad (18)$$

Proof.—Putting $r(t) = Y(t) z(t)$ and substituting in (15), gives

$$Y'z + Yz' = AYz + f. \qquad (19)$$

This gives with (17), $z' = Y^{-1} f$, or

$$z(t) = c + \int_0^t Y^{-1}(s) f\{s, r(s)\} ds.$$

Multiplying the above equation with $Y(t)$ gives the required result (18).

Now we shall prove the following:

THEOREM 6. Let (i) the functions $h_i(t, r_1, \ldots r_n)$ have the property (*);

(ii) the maximal solution $m_i(t)$ is bounded as $t \to \infty$;

(iii) the functions f_i of the vector equation (15) and the matrix $Y(t)$ satisfy the condition

$$\mid Y_i^{-1}(t) \mid \ \mid f_i(t, y_1, \ldots y_n) \mid$$

$$\leqslant h_i \left(t, \frac{\mid y_1 \mid}{\mid Y_1 \mid}, \ \ldots \frac{\mid y_n \mid}{\mid Y_n \mid} \right) \qquad (20)$$

then every solution $r_i(t)$ of (15) satisfies the order relation

$$\mid r_i(t) \mid = 0 \{ \mid Y_i(t) \mid \} \qquad \text{as} \qquad t \to \infty.$$

Proof.—If $r_i(t)$ is the solution of the vector equation (15) then it satisfies, according to the lemma 3, the integral equation

$$r_i(t) = Y_i(t) c_i + \int_0^t Y_i(t) Y_i^{-1}(s) f_i\{s, r_1(s), \ldots r_n(s)\} ds.$$

It then follows from this

$$\frac{\mid r_i(t) \mid}{\mid Y_i(t) \mid} \leqslant \mid c_i \mid + \int_0^t \mid Y_i^{-1}(s) \mid \; \mid f_i\{s, r_1(s), \ldots r_n(s)\} \, ds.$$

We obtain from (20)

$$\frac{\mid r_i(t) \mid}{\mid Y_i(t) \mid} \leqslant \mid c_i \mid + \int_0^t h_i \left[s, \frac{\mid r_1(s) \mid}{\mid Y_1(s) \mid}, \ldots \frac{\mid r_n(s) \mid}{\mid Y_n(s) \mid} \right] ds.$$

An application of Theorem 1 yields

$$\frac{\mid r_i(t) \mid}{\mid Y_i(t) \mid} \leqslant m_i(t) \quad \text{for} \quad 0 \leqslant t < \infty.$$

Since $m_i(t)$ is bounded as $t \to \infty$ according to the assumption, we get the required result

$$\mid r_i(t) \mid = 0\{ \mid Y_i(t) \mid \} \quad \text{as} \quad t \to \infty. \tag{21}$$

Corollary: It now follows from (21) that if we assume the solutions of unperturbed system (16) to be bounded as $t \to \infty$, then every solution of the system (15) is bounded as $t \to \infty$.

We can now formulate a comparison theorem. Consider the differential system in vector form:

$$y' = A(t) y + g(t, y) \tag{22}$$

where $g_i(t, y_1, \ldots y_n)$ are continuous in the region $0 \leqslant t < \infty$, $\mid y_i \mid < \infty$. It is easy to see that the solution $z_i(t)$ of (22), $z_i(0) = c_i$, satisfies the integral equation

$$z_i(t) = Y_i(t) c_i + \int_0^t Y_i(t) Y_i^{-1}(s) g_i\{s, z_1(s), \ldots z_n(s)\} \, ds. \tag{23}$$

THEOREM 7. Let (i) the functions $h_i(t, r_1, \ldots r_n)$ have the property (*);

(ii) the maximum solution $m_i(t)$ is bounded as $t \to \infty$;

(iii) the functions f_i, g_i and the matrix $Y(t)$ satisfy the condition

$$\mid Y_i^{-1}(t) \mid \; \mid f_i(t, y_1, \ldots y_n) - g_i(t, y_1^*, \ldots y_n^*) \mid$$

$$\leqslant h_i \left[t, \frac{\mid y_1 - y_1^* \mid}{\mid Y_1 \mid}, \ldots \frac{\mid y_n - y_n^* \mid}{\mid Y_n \mid} \right];$$

then the difference of any two solutions of systems (15) and (22) respectively satisfies the relation

$$\mid r_i(t) - z_i(t) \mid = 0 \, (\mid Y_i(t) \mid) \quad \text{as} \quad t \to \infty.$$

Proof.—We get from (18) and (23)

$$r_i(t) - z_i(t) = \int_0^t Y_i(t) \; Y_i^{-1}(s) \, [f_i\{s, r_1(s), \ldots r_n(s)\}$$

$$- g_i\{s, z_1(s), \ldots z_n(s)\}] \, ds.$$

The remainder of the proof is similar to that of Theorem 6 and hence omitted.

If we replace the functions $a_{ij}(t)$ by constants a_{ij}, the vectorial equations (15) and (16) are reduced to the following forms considered by Herman Weyl.[6]

$$y' = Ay + f(t, y) \tag{24}$$

and

$$y' = Ay. \tag{25}$$

Then any solution $r_i(t)$ of (24) with $r_i(0) = c_i$ satisfies the integral equation

$$r_i(t) = y_i(t) + \int_0^t z\, Y_i(t-s) f_i\{s, r_1(s), \ldots r_n(s)\}\, ds \tag{26}$$

where $y_i(t)$ is a solution of (25) and $Y(t)$ is a solution of the matrix differential equation:

$$\frac{dY}{dt} = AY; \quad Y(0) = \text{unit matrix}.$$

Further we have

$$|y_i(t)| = |Y_i(t)\, c_i| \leqslant |Y_i(t)|\, |c_i|. \tag{27}$$

Now we can prove the following:

THEOREM 8. Let (i) the functions $h_i(t, r_1, \ldots r_n)$ have the property (*);

(ii) the maximum solution $m_i(t)$ of the system $r_i' = a_i h_i(t, r_1, \ldots r_n)$ through $(0, a_1 |c_1|, \ldots a_n |c_n|)$ has the property

$$m_i(t) = 0\{k_i(t)\} \quad \text{as} \quad t \to \infty$$

where $k_i(t)$ have usual meaning;

(iii) the functions f_i of the vector equation (24) satisfy the condition

$$|f_i(t, y_1, \ldots y_n)| \leqslant h_i(t, |y_1|, \ldots |y_n|); \tag{28}$$

(iv) the solutions of unperturbed system (25) be bounded, i.e.,

$$|Y_i(t)| \leqslant a_i \quad \text{for} \quad t \geqslant 0;$$

then every solution of (24) satisfies the order relation

$$|r_i(t)| = 0\{k_i(t)\} \quad \text{as} \quad t \to \infty.$$

Proof.—If $r_i(t)$ is a solution of (24), it follows from (26)

$$|r_i(t)| \leqslant |y_i(t)| + \int_0^t |Y_i(t-s)|\, |f_i\{s, r_1(s), \ldots$$
$$r_n(s)\}\, ds.$$

From (27) and (28) we obtain

$$|r_i(t)| \leqslant a_i |c_i| + a_i \int_0^t h_i\{s, |r_1(s)|, \ldots |r_n(s)|\}\, ds.$$

An appeal to Theorem 1 gives

$$|r_i(t)| \leqslant m_i(t) \quad \text{for} \quad 0 \leqslant t < \infty.$$

From the assumption (iv) we obtain the required result

$$|r_j(t)| = 0\{k_i(t)\} \quad \text{as} \quad t \to \infty.$$

SECOND ORDER DIFFERENTIAL EQUATIONS

Because of the interest in the second order differential equations, we shall consider similar results below.

Consider the differential equation

$$(r\,y')' + q(t)\,y = f(t, y) \tag{29}$$

and

$$(r\,y')' + p(t)\,y = 0 \tag{30}$$

where $r = r(t)$, $q(t)$, $p(t)$ and $f(t, y)$ are continuous functions in the region $0 \leqslant t < \infty$; $|y| < \infty$. We shall suppose that every solution of (30) is bounded as $t \to \infty$. Then we shall consider the problem when every solution $y(t)$ of (29) satisfies as order relation of the type

$$|y(t)| = 0\{k(t)\} \quad \text{as} \quad t \to \infty \tag{31}$$

where $k(t) > 0$ is continuous in the region $0 \leqslant t < \infty$. Let $y_1(t)$ and $y_2(t)$ be two linearly independent solutions of (30) satisfying

$$r(t)\{y_1(t)\,y_2'(t) - y_2(t)\,y_2'(t)\} = 1. \tag{32}$$

Now we can prove the following:

THEOREM 9. Let (i) the function $h(t, r) \geqslant 0$ be continuous in the region $0 \leqslant t < \infty$, $r > 0$ and non-decreasing in r;

(ii) the maximum solution $m(t)$ of the differential equation $r' = ch(t, r)$ have the property $m(t) = 0\{k(t)\}$ as $t \to \infty$;

(iii) the functions $p(t)$, $q(t)$ and $f(t, y)$ satisfy the condition

$$|\{p(t) - q(t)\}\,y| + |f(t, y)| \leqslant h(t, |y|); \tag{33}$$

then every solution $y(t)$ of (29) satisfies the order relation

$$|y(t)| = 0\{k(t)\} \quad \text{as} \quad t \to \infty.$$

Proof.—Let $y(t)$ be a solution of (29). Then by the method of variation of parameters, $y(t)$ satisfies the integral equation

$$y(t) = c_1 y_1(t) + c_2 y_2(t) + \int_0^t g(s, y)$$

$$\{y_2(t)\,y_1(s) - y_2(t)\,y_2(s)\}\,ds \tag{34}$$

where

$$g(t, y) = \{p(t) - q(t)\}\,y + f(t, y).$$

and c_1 and c_2 are constants.

Suppose

$$| y_2(t) y_1(s) - y_1(t) y_2(s) | \leqslant c \quad \text{for } t > 0, \ s > 0,$$

then it follows from (33) and (34)

$$| y(t) | \leqslant a + c \int_0^t h\{s, | y(s) |\} \, ds$$

where a is a suitable constant.

An appeal to Theorem 1 (for the case $n = 1$) gives

$$| y(t) | \leqslant m(t) \quad \text{for } 0 \leqslant t < \infty.$$

We get because of the assumption (ii).

$$| y(t) | = 0\{k(t)\} \quad \text{as } t \to \infty.$$

Hence the theorem is proved.

Corollary: If $p(t) = q(t)$, we get $f(t, y) = g(t, y)$. Correspondingly the proof of the above theorem implies the boundedness of every solution of $\{r(t) y'\}' + p(t) y = f(t, y)$, given that every solution of $\{r(t) y'\}' + p(t) = 0$ is bounded as $t \to \infty$.

Some of our results are initiated by the results of C. T. Taam.[7, 8] Our results are more general in the sense that the perturbations are majorised by non-linear functions $h_i(t, r_1, \dots r_n)$.

REFERENCES

1. WINTNER, A., 1946, "Asymptotic equilibria," *Amer. Jour. Math.*, **68**, 125–32.

2. VISWANATHAM, B., 1952, "On the asymptotic behaviour of solutions of non-linear differential equations," *Proc. Ind. Acad. Sci.*, **36**, 335–42.

3. LAKSHMIKANTH, V., 1958, "On the boundedness of solutions of non-linear differential equations," *Proc. Amer. Math. Soc.*, **8**, 1044–48.

4. KAMKE, 1932, *Acta mathematica*, **58**, 57–85.

5. WINTNER, A., 1956, "On the non-constant Lipschitz factors in the uniqueness problem of the ordinary differential equations," *Archiv. der. Math.*, **1**, 1–4.

6. WEYL, H., 1946, "Comment of the preceding paper," *Amer. Jour. Math.*, **68**, 7–12.

7. TAAM, C. T., 1954, "The boundedness of the solutions of non-linear differential equations," *Proc. Amer. Math. Soc.*, **5**, 122–25.

8. ———, 1956, "Asymptotic relations between systems of differential equations," *Pac-Jour. Math.*, **6**, 373–88.

9. CODDINGTON, E. A. AND LEVINSON, N., 1955, *Theory of Ordinary Differential Equations*, p. 68.

10. BELLMAN, R., 1953, *The Stability Theory of Differential Equations*, p. 10,

KINETICS OF THE DECOMPOSITION OF AMMONIUM ACETATE IN ACETIC ACID SOLUTION

BY A. S. DEWAGAN AND SAMEER BOSE

(*Department of Chemistry, Mahakoshal Mahavidyalaya, Jabalpur*)

ACETAMIDE is often prepared in the laboratory by the thermal decomposition of ammonium acetate, but the yield is seldom more than 60%. There being no reference in literature to the kinetics of this decomposition, it was felt that such a study might be fruitful. As the reaction involves elimination of a molecule of water, it was carried out in non-aqueous medium in dilute solutions only. The concentration of water produced during the course of the reaction, which was studied to 60% of completion, was not more than 1·5%. Due to the volatility of ammonium acetate and acetic acid the sealed tube technique, as developed by Davies[1] in connection with the esterification of benzyl alcohol with benzoic acid, was followed.

EXPERIMENTAL

Ammonium acetate (prepared by passing ammonia gas into glacial acetic acid) freed from water vapour and Merk's chemically pure glatial acetic acid were used in these experiments.

Estimation of ammonium acetate was done by Sorensen formol titration method, according to Kolthoff[2] where formaldehyde reacts with ammonium salt forming hexamethylene tetramine and liberating an equivalent of the acid which then can be titrated with standard alkali. This happens because hexamethylene tetramine is a very weak base ($Kb = 8 \times 10^{-10}$), hence its salt hydrolyses profusely. Also the base does not act alkaline to phenol red which is used as an indicator.

$$6 \, HCHO + 4 \, CH_3COONH_4 \rightarrow 4 \, CH_3COOH + 6 \, H_2O + N_4(CH_2)_6$$
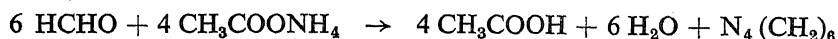
Before estimating the ammonia, the excess of acetic acid was neutralized with alkali to phenol red end point and then excess of formaldehyde solution was added. This method was found to give excellent results for dilute solution of ammonium acetate as already reported by Kolthoff.[3]

Glass ampules (4 c.c. capacity) were thoroughly cleaned with chromic acid, washed, dried and then filled with 1 c.c. of ammonium acetate solution. The solution was carefully introduced without wetting the neck of the ampule which was frozen in ice and cautiously sealed. These were kept in an oil thermostat maintained at the required temperature with an accuracy of $\pm 0.5°$. The ampules were taken out at the desired interval, chilled, broken open and their contents rinsed into a 250 c.c. wide mouth conical flask, in which the ammonium salt was estimated by the method already described.

The results as recorded in Table I reveal that the percentage of ammonium salt decomposed is independent of the initial concentration of the solution. The " Half-life " was also determined by plotting the concentration of the residual ammonium acetate against time which furnished a straight line curve. The " Half-lives " as shown in Table I are practically the same for all the solutions. All these facts point towards a unimolecular order of the reaction. The kinetic constants calculated according to the unimolecular law were found to fall off slightly with time.

TABLE I

Decomposition of ammonium acetate

Time (hrs.)	Initial concentration of ammonium acetate							
	0·6 M		0·9 M		1·0 M		1·2 M	
	Decom-position %	$k \times 10^2$	Decom-position %	$k \times 10^2$	Decom-position %	$k \times 10^2$	Decom-position %	$k \times 10^2$
0	Nil	··	Nil	··	Nil	··	Nil	··
1·5	13·0	9·4	15·9	11·5	15·0	10·8	15·4	11·1
3·0	26·0	10·1	26·0	10·1	27·0	10·5	27·5	10·8
4·5	36·9	10·2	36·5	10·1	37·3	10·4	37·4	10·4
6·5	46·0	9·5	46·2	9·5	46·2	9·5	45·0	9·2
7·5	50·8	9·6	51·0	9·6	50·7	9·4	52·0	9·8
9·0	57·0	8·7	58·0	9·6	57·8	9·6	58·0	9·7
12·0	68·3	9·6	67·5	9·4	68·3	9·6	68·0	9·5
Avrage k	··	9·6		10·0		10·0		10·1
T½ (hrs.)	··	7·35		7·40		7·40		7·20

The experiments were repeated at 120°, 125°, 135°, 140° and 145°, and the average velocity constants were calculated (Table II). The Arrhenious energy of activation was found to be 27·2 k cals. from the slope of the straight line obtained by plotting log k against reciprocal of temperature (Fig. 1).

The falling off, of the reaction rate with time was thought to be due to the retarding effect of the water produced during the reaction. Hence to absorb this water fused sodium acetate was added which produced an acceleration of the reaction rate as recorded in Table III. The energy of activation in presence of 0·5 M solution of sodium and potassium acetates was found to be 22·5 and 22·0 k cals. respectively.

Acetic anhydride was used with the object of converting the water produced into acetic acid. But it seemed to catalyse the reaction because the disappearance of ammonium acetate became very rapid in its presence. The temperature was lowered to 30° at which it took only 90 min. for half decomposition in presence
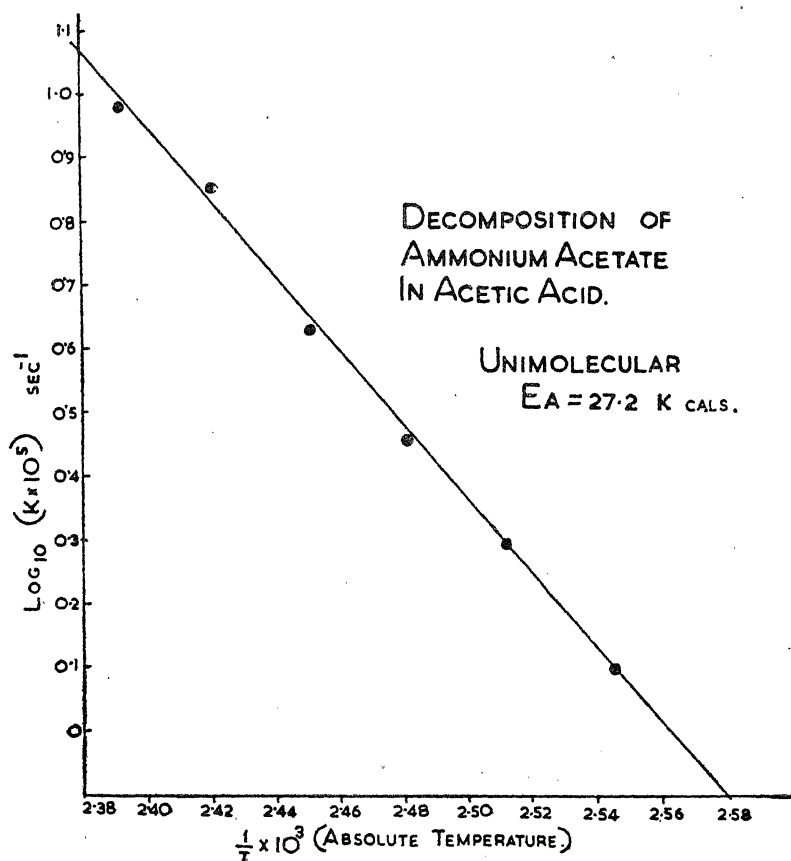
DECOMPOSITION OF
AMMONIUM ACETATE
IN ACETIC ACID.

UNIMOLECULAR
$E_A = 27.2$ K CALS.

FIG. 1

of 10% solution of the anhydride. Unimolecular constants were not obtained as it appeared that some side reactions were also taking place.

DISCUSSION

It is evident that the reaction involves elimination of a molecule of water. Dehydrating agents have an acelerating action on the rate. Hammett[4] has reported that ammonia acts as a strong base in acetic acid and its ionization is practically complete, the reaction being of the type

$$NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-.$$
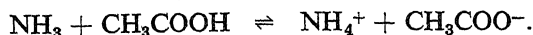
If we assume that a molecule of acetamide is produced by interaction of the two ions then the reaction would become a bimolecular one. But this fact is not borne out kinetically. It is very likely that the minute quantity of unionized ammonium acetate decomposes in the following manner.

$$CH_3-\overset{\overset{\displaystyle O^-}{\|}}{\underset{+}{C}}-OH + NH_3 \rightleftharpoons CH_3-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H_2N \leftarrow H^+}{|}}{C}}-OH \rightarrow H_2O + CH_3CONH_2$$

TABLE II

Variation of k *with temperature*

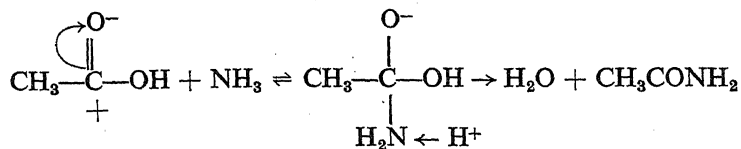| Initial concentration of ammonium acetate		$k \times 10^5$ (min.$^{-1}$) at					
		120°	125°	130°	135°	140°	145°
0·6 M	..	75	128	171	247	419	567
0·9 M	..	76	120	174	262	430	578
1·2 M	..	73	116	167	252	425	560
2·0 M	..	77	110	170	267	431	590
Average k	..	75	118	170	257	426	573

TABLE III

Effect of sodium acetate on k *at* 130°

k (min.$^{-1}$) in absence of sodium acetate = 166
(1·0 M ammonium acetate + 1·5 M sodium acetate)

Time (min.)	Decomposition (%)	k (min.$^{-1}$)
0	Nil	..
66	15	246
120	21·7	204
180	32·4	218
300	45·3	201
480	63·0	207
660	73·4	200
Average	..	212

The reaction depends on the polarization of the carbonyl group which provides the centre for the nucleophylic attack by NH_3 at the carbon atom of the carboxyl group. There is evidence for a similar reaction occurring during amide formation

by the ammonolysis of an ester studied by Day[5] and Hammett[6] where an intermediate complex of the following type has been visualized.

$$CH_3\text{---}\overset{\overset{\displaystyle O^-}{\mathrm{C}}}{\underset{\underset{\displaystyle H \rightarrow NH_2}{|}}{|}}\text{---}OCH_3$$
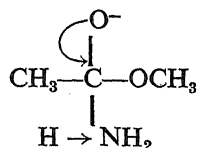
In the ammonolysis reaction also the bimolecular velocity constants showed a slight downward drift which has been accounted for by Hammett by assuming that the amide produced acted as a negative catalyst.

The downward drift with time in the velocity of the present reaction might be due to the diminution in the percentage of the unionized ammonium acetate as the concentration of the salt falls with the progress of the reaction. It is also very likely that the water produced, facilitates the reversal of the reaction.

Thanks of the authors are due to Principal Dr. R. L. Nirula and to Dr. V. Gore, Professor of Chemistry for all the facilities provided for this work.

SUMMARY

The decomposition was studied between 120° and 145° by heating in sealed tubes, one c.c. of moisture-free solution of ammonium acetate and following it by estimating the ammonium content. From " half-life " measurements it was found to be a unimolecular reaction but the velocity constants drifted slightly downwards with time. Log k when plotted against reciprocal of temperature yielded a straight line, the slope of which furnished the energy of activation (27·2 k cals.). Sodium and potassium acetates were found to increase the rate and lower the energy of activation.

REFERENCES

1. DAVIES, M. M., 1937, *Trans. Faraday Soc.*, **33**, 331.

2. KOLTHOFF, I. M., 1921, *Pharm. Weekbland.*, **58**, 1463.

3. —— AND STENGER, V. A., 1947, *Volumetric Analysis*, **2**, 158 (Interscience Publishers, New York).

4. HAMMETT, L. P., 1940, *Physical Organic Chemistry* (McGraw-Hill Book Co., New York).

5. DAY, A. R., GORDON, M. AND MILLER, J. G., 1958, *J. Amer. Chem. Soc.*, **70**, 1946.

6. HAMMETT, L. P. AND BETTS, R. L., 1937, *ibid.*, **59**, 1568.

SOILS OF WEST BENGAL*

Part III. District—24 Pargonas.

By S. K. MUKERJI

(Agricultural Chemist, West Bengal)

THIS district lies in the extreme eastern flank of the River Bhagirathi within the parallels 21° 31′ and 23° 15′ North latitude and 88° 2′ and 89° 6′ East longitude. It has an area of 5292·8 square miles.

The northern tract is a land of sluggish or stagnant rivers whose beds are often out of reach of the scour of head water or deposition due to the tides; and of inland depressions which have not been filled up because of rivers which should perform this office, are locked up into their channels by the high banks of silt which they have deposited.

The southern tract on the other hand is a network of tidal channels, rivers, creeks and islands. Some of these islands are mere swampy marshes covered with low forests and scrub wood jungles, but those to the north, which are embanked grow rich crops of rice. As one approaches the coast, the land gradually declines to an elevation which throughout many hundred square miles is scarcely raised above high water mark.

The forest area is a wide stretch of low forest with trees rising to a height of about 30–35 feet.

The maximum recorded height above sea-level is 31 feet in the Police Station Mahestola and the minimum is 12 feet in the Police Station Kakdwip. Though large tracts exist where the level is below the sea-level which are either prevented by embankments or high ridges from submergence. The landmass of 24 Pargonas are situated between two rivers, the Bhagirathi and the Ichamati both in their turn being the old channels of the Ganges. The land in between has a restricted drainage and drain into the different tidal creeks through sluices which are gradually being filled up due to tidal deposits.

Average rainfall of the district	.. 63·76″
Number of rainy days ..	.. 83·9
Average temperature of the district ..	80·3° F.
Langs factor	.. 60·4
Meyers N-S-Q- Av.	.. 283·25
Average barometric factor for barometric cistern above mean sea-level ..	21

The average area under main crops are given in acres:

Aus	..	141,087·87	Aman ..	1304,237·49
Sugarcane	..	1,650·8	Jute ..	35,390·17

The langs factor is 60·4. This favours formation of brown earth group of soils which are often found here in the riverine ridges. The Meyers N–S quotient is (390·7 to 175·8) 283·25 which favours formation of brown forest soils and degraded types of soils. The Sundarban soils, however, are grey to greyish black in colour and the saline soils met with in this area are at many places degraded on the surface. The following are the natural soil regions found in the district formed as a result of the physical features, watershed and climate. The parent materials are (1) Ganga alluvium and (2) Salinised Ganga alluvium.

The direct deposits of Ganga alluvium, which are salt free and rich in diva-ients. The Ganga alluvium differ in their composition in different periods. Some-times they are rich in calcite, at other times rich in dolomite and sometime rich in magnesite. The soils formed from these different kinds of parent alluvium still retain their identity.

The indirect deposits are Ganga alluvium going into the sea are returned back by tides and are redeposited in the esturian region as alluvium very rich in salts. The silt and clay loads carried down into the sea beyond the delta undergo partial transformation in their exchange complex due to the exchange reaction with sodium chloride of sea-water. During tides, these constituents in suspension rush back through the numerous tidal creeks in the coastal region and get partially deposited, due to gravitational force becoming greater than the force of suction exerted by ebb water, in the flood plains situated inland. The muddy waters of the sea in the approaches (to an extent of about 50 miles) in the mouth of the Ganges, in the Bay of Bengal give us an idea of the magnitude of the alluvium involved. The following soil-forming factors are recognised to act upon these deposits.

Salinised soil, deposited by tidal back action during ebbs are subjected to two principal soil-forming agencies:

1. Rain water, and

2. Sea-water.

Rain water brings about the following changes in the nature of the tidal deposits as a result of leaching under different environmental conditions:

1. (*a*) Salts in the soil get partially leached away which if proceeds in the absence of dolomite or calcite in the original deposit, produce due to the sodium ion entering the exchange complex in the presence excess of salts *Saline alkali soil.*

(*b*) If however salts get completely leached away, during leaching sodium enters the exchange complex and the product in *Non-saline alkali soil.*

(*c*) If this process of leaching takes place in the presence of calcite, dolomite or magnesite in the parent deposit, *Normal soil results.*

(*d*) If this process takes place in the presence of buried half decomposed organic matter hydrogen ion from organic acids also take part in the formation of these soils and produce, Degraded alkali soil (Saline Turf Soils).

2

2. Leaching by sea-water makes sodium to enter the exchange complex and produces Saline alkali soils as well.

Thus as a result of variations in parent alluvium, in land features and situation, a pattern of the following unlike soils have been formed.

1. *Non-saline soils*

    (*a*) Ganga riverine soils.

    (*b*) Ganga flat land soils.

    (*c*) Ganga low land soils.

2. *Coastal soils of Tidal origin*

    (*a*) Dolimite phase }
    (*b*) Magnesite phase }   (*a*) Saline soils.

    (*a*) Tidal phase }
    (*b*) Non-tidal phase }   (*b*) Saline alkaline soils.

                        (*c*) Non-saline alkali soils.

                        (*d*) Degraded alkali soils (Saline turf soils).

DESCRIPTION AND OCCURRENCE

A brief description of the above soil associations and their phases are given below, and the positions of different soil associations have been indicated in the tentative map of the district (Fig. 1).

(1) *Ganga riverine soils.*—These are formed of soils on recent alluvial fans, flood plains or other secondary deposits, having undeveloped profiles and underlain by unconsolidated material. These profiles show no accumulation of clay or lime in the subsoil resulting in weathering and downward movement of water from surface horizon. Deposits of alluvium having different texture in different layers in an unsystematic manner is evident. The soils of this association examined occur in the police stations of:

P. S. Kanchrapara	..	Entire part.
P. S. Jagaddal	..	Entire part.
P. S. Amdanga	..	Entire police station except the part lying north of the road from Naihati to Bangaon through Habra.
P. S. Habra	..	In the south-east corner.
P. S. Baraset	..	Whole of the police station except the north-eastern part of the police station lying north of the Baraset to Basirhat railway line and east of the Sunti Nadi.
P. S. Deganga	..	Entire police station except the north-eastern part lying north-east of the road from Ichhapur to Chaura and north of the Padma Nadi.
P. S. Baduria	..	Area lying in between the road from Dakshin Chatra where it crosses the Padma River to the ferry ghat on the Ichhamati and the road

		from Adurhati to the ferry ghat and the tributary of the main Ichhamati River.
P. S. Basirhat	..	Whole of Basirhat except south-western portion of the police station lying south of a line joining Jagatpur and Ramachandrapur and west of the stream which falls into Bidyadhari.
P. S. Hasnabad	..	Northern part of the police station bounded by a small stream a road from Sadibgachi to Murarisaha and another stream on the south (both of the streams are tributaries to River Dansa.
P. S. Swarupnagar	..	The area lying between the main Sonai Khal and its branch to the South of the main canal.
P. S. Bagdaha	..	Whole of the police station except the area west of the Chhalakatha Khal and Buruni Bil.
P. S. Bangaon	..	The area lying to the west of Talkola Bil, Chaite Khal, Belta Bil, Ramchandrapur Bil and west of the embankment which runs from Bangaon to Gobrapur and Kundipur Bangar.
P. S. Gaighata	..	A small portion to the east of the road which runs from Panchapota Jhandanga and east of Beri Bangar.
P. S. Baranagar	..	The portion of the police station lying to the west of the railway line.
P. S. Baruipur	..	The area lying west of the Railway line from Sonarpur to Mathurapur except the north-eastern part lying north of the road from Chandpur to Chingripota.
P. S. Kulpi	..	The area bounded by Hara Khal, Banai Khal, Manteswar Khal and River Hooghly.
P. S. Magrahat	..	A small portion to the south of the police station bounded by the Magra-Jainagar Khal, Mandirbazar Khal and the railway line.

(2) *Ganga low lands.*—This is comprised of soils on lower plains, depressions, left river beds, having a good accumulation of clay in the surface soil, underlain by unconsolidated material more often riverine profile. Buried organic peat or thick organic layer composed of partially decomposed buried plant materials are also met with at different depths. These are clay pan soils, in which pans are relatively near the surface and relatively impervious to the downward movement of water. Water moves through big cracks in the soils. This is underlain by a horizon at places lime, or lime iron, over deeply laid partially decomposed buried organic plant residues, which do not soften or disintegrate in water. This again is underlain by riverine profile. Soils of this association occur in the following police stations:

P. S. Naihati	..	The entire police station.
P. S. Amdanga	..	The area lying north of the road from Naihati to Bongaon with Napara.
P. S. Habra	..	Whole of Habra Police Station except the small area lying south of the River Bidyadhari to the south-west of the police station.
P. S. Baduria	..	The area lying north-west of the road from Dakshin Chatra to the ferry ghat.
P. S. Dumdum	..	The entire police station except the marshy land to the south of B.B. Light Railway line.
P. S. Bagdaha	..	A small portion to the south-eastern part of the police station bounded by the Betna River Kodia Nadi and Sundra Bangar.
P. S. Bongaon	..	Area lying to the east of the embankment from Ghatbangar to Golrapur and south of the line joining Padma Bil and Gobrapur, and another small portion lying in between and comprising bil area of Jessore Road. Bara and Chota Jchala Bil, Belta and Talkola Bil.
P. S. Gaighata	..	The whole of the area lying to the west of the Railway line (E. Railway).
P. S. Rajarhat	..	A small portion lying to the north of B.B. Light Railway line.
P. S. Sonarpur	..	The portion lying in the area north of the Railway line from Calcutta to Canning.
P. S. Baruipur	..	The area bounded by Railway line (Canning line and Lakshmi Kantapur branch line) on two sides and police station boundary and the Pyali River on the south and the east.

(3) *Saline soils.*—This is comprised of soils which have been deposited due to backtides over the old flood plains in the river beds, river courses, creeks and land depressions. These are of more recent origin. These soils occur in the following police stations:

P. S. Rajarhat	..	Whole of the area lying south of the B.B. Light Railway.
P. S. Tollygunge	..	The area lying west of the Tolly's Nala.
P. S. Behala	..	The entire area except a small portion lying to the east of Kaorapukur Khal.
P. S. Mahestala	..	The entire police station.
P. S. Budge Budge	..	The entire part of the police station.
P. S. Falta	..	The whole of Falta police station.
P. S. Diamond Harbour	..	The whole of the police station.

P. S. Sandeshkhali	..	Northern part of the police station. The southern boundary of which is made by a number of streams—from Bargan Gopalpur to Lankhali and from Rajbari to ferry ghat on Chhota Kalagachhi Khal and a small portion lying in the area south of the Bidyadhari River and the Buinjali Nadi.
P. S. Haroa	..	North and north-eastern part of the police station area lying north of the line joining approximately Talbaria and Khasbalanda and the north-east of the stream which takes off from the Bidyadhari near Mohanpur.
P. S. Magrahat	..	Whole of Magrahat Police Station except a small portion to the south bounded by Mandir Bazarkhal Magra to Joynagarkhal and the Railway line.
P. S. Hasnabad	..	The whole area lying west of the River Dansa and also strip of land lying to the west of the River Sahebkhali Gumti Nadi and the Raimangal River.
P. S. Canning	..	The area bounded by Seoli Nadi on the north Kasati and Matla on the west and Matla on the south.
P. S. Sonarpur	..	The area lying north-east of the Canning line.

(4) *Saline alkali soils.*—These soils have been deposited by back tides in depressions, flood plains and river beds. Interactions between the parent deposit and the saline tidal back-rushas are yet incomplete. They occur in police station of:

P. S. Sagar	..	The entire police station.
P. S. Kakdwip	..	The area lying south of the Kalnagini Khal and Ghugudanga River.
P. S. Kulpi	..	South-western most part of the police station bounded by the Manteswar and the Jhikra Khal.
P. S. Mathurapur	..	Area lying south of the line made by the Saralda Khal, Sutarbag River, Chhatua River, Raidighi River and Chuprijhara River.
P. S. Canning	..	The whole area except east of the River Malta and Beledona River except the area lying to the east of Pathankhali and Rupkhali Khal and south of Atharabaki and Char Bidya Khal.
P. S. Sandeshkhali	..	The area lying in between the line made by a number of streams, from Chunchura to Lankahi again from Rajbari to the ferry ghat on the Chhota Kalagachhi Khal and another tributary to River Dansa in the north and Hatakhali Nadi, Boalia Gung, Jushkhali Khal and the Raimangal River in the south of the east.

(5) *Non-saline alkali soils.*—At places the tidal deposits took place on places where sufficient calcium was not present to prevent sodium getting into the exchange complex or where calcium got replaced during the process of leaching by sodium chloride. This has led to the production of a soil where exchange complex has more than 15 per cent. sodium. These soils have been formed as alkali soils. These are found in:

P. S. Bhangar	..	The area lying north of Kata Khal and west of Krishnapur Canal.
P. S. Baraset	..	The area lying south-east of B.B. Light Railway.
P. S. Swarupnagar	..	Entire part of the police station except the area west of the Gazana Baour and the area bounded by the Sonai Khal and one of its branch.
P. S. Mathurapur	..	A considerable portion of the police station is under saline soils and saline alkali soils. The boundaries have been delineated by a number of small stream courses and canals, *viz.*, small streams in the north, Moni River, Thakuran River, Chuprijhara, Moni River, Raidighi Nadi, Chatna River, Sutarbag Khal, Sasalda Khal, Koloa Khal, Jorabaria Khal and Batapukuria Khal on the other sides.

(6) *Degraded saline alkali soils.*—Leaching of these soils specially in the presence of the decomposing vegetation within 4 to 6 feet of the surface has led to the formation of acidity. The organic acids and high salt contents have jointly acted upon the tidal deposit and have formed the saline unsaturated soils termed as above. This soil tract occurs in:

P. S. Sandeshkhali	..	The area south of the Hatakhali Nadi, Boaliagunj, Jushkhali Khal and north of the Bidya River and Puinjali River.
P. S. Canning	..	A small portion to the north-east of the police station bounded by Hanakhal, Rup Khal, Atharbaki Khal, Char Bidya Khal, Hatakhali and Suryabaric Khal.

(7) *Ganga flat land.*—These are formed of soils on young alluvial flats or other secondary deposits. The profiles are slightly developed.

P. S. Bagdah	..	The area lying west of the Chhala Katha Khal and Buruni Bil.
P. S. Bangoan	..	A small portion in the north bounded by the Kodia Nadi, the road which runs from Bangaon to the north and the line joining the Padma Bil and Golrapur. The area lying south of the road running east-west from Gopalnagar where it crosses the railway line to the east where it enter the Pakistan territory.
P. S. Gaighata	..	The whole area to the east of the Eastern Railway line except a small portion to the east of road running from Panchpota to the north.

PHYSICAL CHARACTERISTICS OF THE SOIL ASSOCIATION

(*Family:* Ganga family of soils)

Series	Ganga Riverine	Ganga Low Land
Profile development	Immature	Lacustriene
Colour	Pale Olive 5Y 6/3 to Olive 5Y 5/3 to Pale Yellow 5Y 7/3	Olive Grey 5Y 5/2 to Dark Grey 5Y 4/1
Concretions	Nil to very few small in size	Very small gritty particles of dolomatic nature
Layerisation	Distinct irregular alluvial layers	Clean heavy layers
pH	7·0 to 8·65	7·6 to 8·2
Lime as carbonate	1 to 7 per cent.	1 to 4 per cent.
Sesquioxide	Immobile	Immobile
Clay percentage	Average to low	High on top decreases with depth

(*Family:* Coastal soils of tidal origin-estuaian areas)

Series	Saline soils	Saline alkali soil	Non-saline alkali	Degraded saline soil
Profile development	Immature	Immature	Immature	..
Colour	Olive 5Y 5/3 to Dark Grey 5Y4/1	Pale Olive 5Y 5/4	Olive 5Y 5/4	Olive 5Y 5/2 to Dark Grey 5Y 4/1
Concretions	Nil	Nil	Nil	Nil

(*Family:* Coastal soils of tidal origin-estuarian areas)—*Contd.*

Series	Saline soils	Saline alkali soil	Non-saline alkali	Degraded saline soil
Layerisation	Nil	Clean layers of deposit on different dates	Nil	Clean layers
pH	6·5 to 7·8	7·4 to 9·0	7·2 to 8·3	4·3 to 7·0
Lime as carbonate	(1) No lime (2) lime present in fine form (3) Magnesite present	(1) No lime (2) Lime in fine form or small concretions	(1) No lime	No lime
Sesquioxide	Immobile	Immobile	Immobile	Slightly mobile
Clay percentage	Average to high	High and uniform	Average to high	Average to high
Salinity percentage	0·2 to 1·8	0·38 to 1·2	0·1 to 0·09	0·6 to 1·2
% saturation of monovalents in exchangeable basis.	12 to 11	55 to 40	45 to 30	17·5 to 10

SUMMARY

1. The soils of this district have been divided into two families, (*a*) Ganga family of soils and (*b*) Coastal family of soils.

2. The coastal soils could be divided into four different series, occurring in blocks. They are saline soils, saline alkali soils, alkali soils and degraded saline alkali soils.

3. The Ganga family soils had three series, the Ganga riverine series, the Ganga flat land series and the Ganga low land series.

4. The distribution of these series has been indicated in the map.

5. General chemical and morphological nature and the genesis have been discussed.

ACKNOWLEDGEMENT

SOIL ASSOCIATION MAP OF
24 PARGANAS (TENTATIVE)
WEST BENGAL

5 2 0 5 10
SCALE

+ +	GANGA RIVERINE
////	,, LOWLANDS
≡	,, FLATLANDS
× ×	SALINE SOILS
ᴗ ᴗ	DEGRADED ALKALI SOILS
Δ Δ	NON-SALINE ALKALI SOILS
V V	SALINE ALKALI SOILS

N

88 30
89 00

23 00
22 30

EAST PAKISTAN

MIDNAPUR.

BAGDHA
GAON
BIJPUR
NAIHATI
GAIGHATA
JAGADDAL
AMDANGA
HABRA
NOAPARA
SWARUPNAGAR
BARRACKPUR
BARASAT
BADURIA
KHARDAH
DEGANGA
DUMDUM
BASIRHAT
RAJARHAT
LHAROA
HASNABAD
METIABURJ
ALIPORE
BHANGOR
MANESTALA
BEHALA
TOLLYGUNGE
BUDGEBUDGE
BISHNPUR
BARUIPUR
SANDESKHALI
FALTA
CANNING
MAGRAHAT
DAIMONOHARBOUR
JAINAGAR
KULPI
KAKDWIP
SUNDAR BANS
SAGAR

B A Y   OF   B E N G A L

S. K. HALDAR.

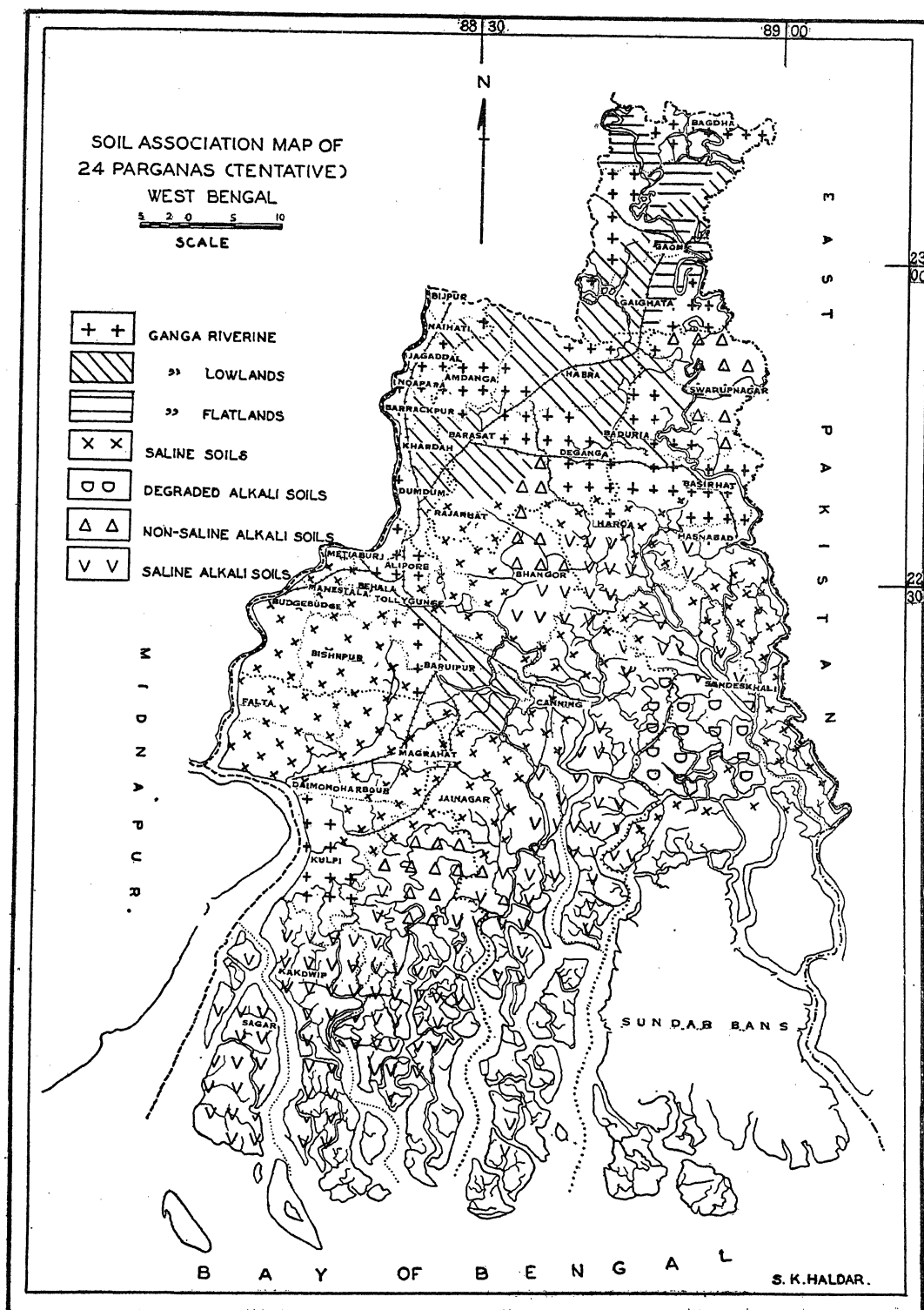FIG. 1

ON THE MAXIMUM TERM OF AN ENTIRE DIRICHLET SERIES

By K. N. Srivastava

(*Department of Mathematics, University of Allahabad*)

1. Let us put

$$f(s) = \sum_{n=1}^{\infty} a_n e^{\lambda_n s} \qquad \text{(where } s = \sigma + \iota t),\qquad (1.1)$$

where

$$0 < \lambda_1 < \lambda_2 \ldots \ldots < \lambda_n \to \infty$$

$$\lim \inf. \ \lambda_{n+1} - \lambda_n = h > 0, \ \ D \leqslant \frac{1}{h}$$

and 'D' is the upper density of the sequence $\{\lambda_n\}$, which is supposed to be finite.

Let 1.1 be convergent (necessarily absolutely convergent, since $D \leqslant 1/h$) in the whole plane, hence $f(s)$ represents an entire function. For this class of functions for any given $Rl \ s = \sigma$, $\underset{-\infty < t < \infty}{\text{Max}} |f(\sigma + \iota t)|$ has a finite value $M(\sigma)$. Let ρ be the order and λ be the lower order of $f(s)$ in sense of Ritt.

Let $\mu(\sigma)$ be the maximum term and $\lambda_{N(\sigma)} = \lambda_N$ be the indicative index of the maximum term corresponding to $Rl \ s = \sigma$.

The absolute convergence of (1.1) in the whole plane requires

$$\lim \sup_{n \to \infty}. \ \frac{\log |a_n|}{\lambda_n} = -\infty.$$

As pointed out by Y. C. Yung[1], we may construct a Newton's polygon with the verticies at the points whose co-ordinates are $(\lambda_n, -\log |a_n|)$. Following the method of Valiron,[2] as in the case of Taylor's series, we get

$$\log \mu(\sigma) = \log \mu(\sigma_0) + \int_{\sigma_0}^{\sigma} \lambda_{N(t)} \, dt. \qquad (1.2)$$

As a direct consequence of this result, K. Sugimura[3] and Q. I. Rehman[4, 5] have proved.

$$\rho = \lim \sup_{n \to \infty}. \ \frac{\log \log \mu(\sigma)}{\sigma} = \lim \sup_{\sigma \to \infty}. \ \frac{\log \lambda_{N(\sigma)}}{\sigma} \qquad (1.3)$$

$$\lambda = \lim \inf_{\sigma \to \infty}. \ \frac{\log \log \mu(\sigma)}{\sigma} = \lim \inf_{\sigma \to \infty}. \ \frac{\log \lambda_{N(\sigma)}}{\sigma}. \qquad (1.4)$$

Since ' D ' is finite, according to K. Sugimura[3] for $0 \leqslant \rho < \infty$, we have

$$\log \mu (\sigma) \sim \log M (\sigma).$$

1.2. forms the fundamental basis of all the results proved in this note.

2. THEOREM 1.—For an entire Dirichlet series of finite order we have

$$(i) \quad \lim\sup_{\sigma \to \infty} \frac{\log \mu (\sigma)}{\lambda_{N(\sigma)}} \geqslant \frac{1}{\lambda} \qquad 0 \leqslant \lambda < \infty \qquad (2.1)$$

$$(ii) \quad \lim\inf_{\sigma \to \infty} \frac{\log \mu (\sigma)}{\lambda_{N(\sigma)}} \leqslant \frac{1}{\rho} \qquad 0 \leqslant \rho < \infty. \qquad (2.2)$$

To prove this theorem we require following lemma.

LEMMA 1.— (i) Let $\chi (X)$ be a real function, positive and integrable ' L ' in any finite interval $(\triangle, x)$ where

(ii) $\chi (X) \geqslant 1$ for all large ' X ',

(iii) $\lim\sup_{X \to \infty} \frac{\log \chi (X)}{X} = A, \quad \lim\inf_{X \to \infty} \frac{\log \chi (X)}{X} = B$

(iv) $I (X) = \int_{\triangle}^{X} \chi (t) \, dt,$

then

$$\lim\inf_{X \to \infty} \frac{I (X)}{\chi (X)} \leqslant \frac{1}{A} \leqslant \frac{1}{B} \leqslant \lim\sup_{X \to \infty} \frac{I (X)}{\chi (X)}.$$

The proof of this lemma is similar to that of Dr. Shah.[6] We shall show

$$\lim\inf_{X \to \infty} \frac{I (X)}{\chi (X)} \leqslant \frac{1}{A}.$$

Proof.—Lemma is certainly true for $A = \infty$, hence we consider the case when A' is finite and $A \geqslant 0$. Suppose first that $A > 0$, and let the lemma be false, so that we have $I (X) > C\chi (X)$, for all $X > \delta_0 = \delta (C) > X_0$ where $C = 1/A$ is a positive constant. Since

$$I (X) = \int_{\triangle}^{X} \chi (t) \, dt$$

I' (X) exist and is equal to $\chi (t)$ almost everywhere. Hence

$$\frac{I' (X)}{I (X)} < C$$

almost everywhere in (δ, ∞), hence for all large ' X '

$$\log I (X) = \log I (\delta) + \int_{\delta}^{X} \frac{I' (X)}{I (X)} < \log I (\delta) + \frac{X - \delta}{C}.$$

or

$$\log \chi (X) + \log C < \log \xi (\delta) + \frac{X - \delta}{C},$$

hence

$$\lim_{X \to \infty} \sup . \frac{\log \chi (X)}{X} < \frac{1}{C} = A,$$

which contradicts the hypothesis. Hence the lemma is proved. If $A = 0$, then we take 'C' to be a large constant.

Proof of the theorem.—We have

$$\log \mu (\sigma) = \log \mu (\sigma_0) + \int_{\sigma_0}^{\sigma} \lambda_{N(t)} \, dt$$

taking $\chi (\sigma) = \lambda_{N(\sigma)}$ and $I (\sigma) = \log \mu (\sigma)$ in the above lemma we get the result.

Alternatively.—Let

$$\lim_{\sigma \to \infty} \sup . \frac{\log \mu (\sigma)}{\lambda_{N(\sigma)}} = A$$

then

$$\log \mu (\sigma) < (A + \epsilon) \lambda_{N(\sigma)} \quad \text{for} \quad \sigma > \sigma_0, \quad \epsilon > 0,$$

also

$$\log \mu (\sigma) = \log \mu (\sigma_0) + \int_{\sigma_0}^{\sigma} \lambda_{N(t)} \, dt$$

so that

$$\frac{\mu' (\sigma)}{\mu (\sigma)} = \lambda_{N(\sigma)}.$$

except for a set of measure zero, where $\mu' (\sigma)$ is the derivative of $\mu (\sigma)$. Hence

$$\frac{\mu' (\sigma)}{\mu (\sigma) \log \mu (\sigma)} > \frac{1}{(A + \epsilon)}.$$

Integrating

$$\log \log \mu (\sigma) > \frac{\sigma}{A + \epsilon} + \text{constant},$$

or

$$\lim_{\sigma \to \infty} \inf . \frac{\log \log \mu (\sigma)}{\sigma} \geqslant \frac{1}{A},$$

so that

$$\lambda \geqslant \frac{1}{A}.$$

Similarly for (*ii*), we set:

$$\liminf_{\sigma \to \infty} \frac{\log \mu(\sigma)}{\lambda_{N(\sigma)}} = A_1,$$

then as before

$$\log \mu(\sigma) > (A_1 - \epsilon) \lambda_{N(\sigma)} \quad \text{for} \quad \sigma > \sigma_0, \quad \epsilon > 0,$$

or

$$\frac{\mu'(\sigma)}{\mu(\sigma) \log \mu(\sigma)} < \frac{1}{A_1 - \epsilon}.$$

Integrating

$$\log \log \mu(\sigma) < \frac{\sigma}{A_1 - \epsilon} + \text{constant.}$$

$$\liminf_{\sigma \to \infty} \frac{\log \mu(\sigma)}{\lambda_{N(\sigma)}} \frac{\log \log \mu(\sigma)}{\sigma} \leqslant \frac{1}{L} \leqslant \frac{1}{\iota} \quad \limsup_{\sigma \to \infty} \frac{\log \mu(\sigma)}{\lambda_{N(\sigma)}} \frac{\log \log \mu(\sigma)}{\sigma},$$

since $\mu(\sigma) \leqslant M(\sigma)$ and by hypothesis $\log \mu(\sigma) \sim \log M(\sigma)$, we have the result.

It is possible to prove

$$\liminf_{\sigma \to \infty} \frac{\log \mu(\sigma)}{\lambda_{N(\sigma)}} \frac{\iota_2 \mu(\sigma) \ldots \ldots \iota_k \mu(\sigma)}{\sigma \iota_1(\sigma) \ldots \ldots \iota_{k-2}(\sigma)} \leqslant \limsup_{\sigma \to \infty} \frac{\iota_{k+1} \mu(\sigma)}{\iota_{k-1}(\sigma)}$$

$$\limsup_{\sigma \to \infty} \frac{\log \mu(\sigma)}{\lambda_{N(\sigma)}} \frac{\iota_2 \mu(\sigma) \ldots \ldots \iota_k \mu(\sigma)}{\sigma \iota_1(\sigma) \ldots \iota_{k-2}(\sigma)} \geqslant \liminf_{\sigma \to \infty} \frac{\iota_{k+1} \mu(\sigma)}{\iota_{k-1}(\sigma)}$$

where $\iota_k = \log \log \ldots \ldots \log k$ times.

THEOREM 3.—If $L(X)$ be any logarithmico-exponential function (3, pp. 17) tending to infinity with ' X ' and let

$$\lim_{\sigma \to \infty} {\sup \atop \inf} \frac{\log \log \mu(\sigma)}{L(\sigma)} = \frac{M}{m},$$

then

$$\liminf_{\sigma \to \infty} \frac{\log \mu(\sigma)}{\lambda_{N(\sigma)}} L'(\sigma) \leqslant \frac{1}{M} \leqslant \frac{1}{m} \leqslant \limsup_{\sigma \to \infty} \frac{\log \mu(\sigma)}{\lambda_{N(\sigma)}} L'(\sigma), \qquad (2.5)$$

$L'(\sigma)$ is the derivative of $L(\sigma)$.

Corollary 1.—If

$$\log \log \mu(\sigma) = [1 + 0(1)] \log \sigma.$$

then

$$\lim_{\sigma \to \infty} \frac{\log \mu (\sigma)}{\lambda_{N(\sigma)}} \frac{1}{\sigma} = 1.$$

(2.6)

Corollary 2.—If

$$\log \mu (\sigma) \sim k \cdot \lambda_{N(\sigma)} \cdot \sigma \quad (o \leqslant k \leqslant 1), \text{ then}$$

(2.7)

$$\lim_{\sigma \to \infty} \frac{\log \log \mu (\sigma)}{\log (\sigma)} = \frac{1}{k}.$$

(2.8)

Corollary 1 shows that for a given class of function we have a precise relation (2.6). It is not possible to improve the hypothesis $\log \log \mu (o) = [1 + 0 (1)] \log \sigma$, for, given any positive constant β, we can construct a function $f(s)$ for which

$$\log \log \mu (\sigma) = [1 + \beta + 0 (1)] \log \sigma$$

for all $\sigma > \sigma_0$ and for which

$$\lim_{\sigma \to \infty} \frac{\log \mu (\sigma)}{\lambda_{N(\sigma)} \cdot \sigma} = \frac{1}{1 + \beta} < 1.$$

Take for instance

$$f(s) = \sum_{1}^{\infty} \frac{e^{ns}}{n^{n\alpha}}, \quad \alpha = \frac{1 + \beta}{\beta}.$$

Proof.—Let

$$\limsup_{\sigma \to \infty} \frac{\log \mu (\sigma)}{\lambda_{N(\sigma)}} L' (\sigma) = B,$$

then

$$\frac{\log \mu (\sigma)}{\lambda_{N(\sigma)}} L' (\sigma) < (B + \epsilon) \quad \text{for} \quad \sigma > \sigma_\epsilon, \ \epsilon > 0,$$

also from

$$\log \mu (\sigma) = A + \int_{\sigma_\epsilon}^{\sigma} \lambda_{N(t)} \, dt,$$

we have

$$\frac{\mu' (\sigma)}{\mu (\sigma)} = \lambda_{N(\sigma)}$$

except for a set of measure zero, where $\mu' (\sigma)$ is the derivative of $\mu (\sigma)$, so that

$$\frac{\mu' (\sigma)}{\mu (\sigma) \cdot \log \mu (\sigma)} > \frac{L' (\sigma)}{B + \epsilon},$$

integrating

$$\log \log \mu \ (\sigma) > \frac{L \ (\sigma)}{B + \epsilon} + \text{constant,}$$

hence

$$\lim_{\sigma \to \infty} \inf. \frac{\log \log \mu \ (\sigma)}{L \ (\sigma)} \geqslant \frac{1}{B} \ .$$

Similarly set

$$\lim_{\sigma \to \infty} \inf. \frac{\log \mu \ (\sigma)}{\lambda_{N(\sigma)}} L' \ (\sigma) = B',$$

hence

$$\frac{\log \mu \ (\sigma)}{\lambda_{N(\sigma)}} L' \ (\sigma) > (B' - \epsilon) \quad \text{for} \quad \sigma > \sigma_\epsilon, \ \epsilon > 0,$$

or

$$\frac{\mu' \ (\sigma)}{\mu \ (\sigma) \log \mu \ (\sigma)} < \frac{L' \ (\sigma)}{B' + \epsilon},$$

integrating

$$\frac{\log \log \mu \ (\sigma)}{L \ (\sigma)} < \frac{1}{B' - \epsilon} + \frac{\text{constant}}{L \ (\sigma)},$$

therefore

$$\lim_{\sigma \to \infty} \sup. \frac{\log \log \mu \ (\sigma)}{L \ (\sigma)} \leqslant \frac{1}{B'},$$

or

$$B' \leqslant \frac{1}{M} \ .$$

3. THEOREM 4.—For an entire Dirichlet series $f(s)$, if $0 < \sigma_1 < \sigma_2$, then

$$\left(\frac{e^{\sigma_2}}{e^{\sigma_1}} \right)^{\lambda_{N(\sigma_1)}} \leqslant \frac{\mu \ (\sigma_2)}{\mu \ (\sigma_1)} \leqslant \left(\frac{e^{\sigma_2}}{e^{\sigma_1}} \right)^{\lambda_{N(\sigma_2)}}. \tag{3.1}$$

Proof.—

$$\mu \ (\sigma_1) = | \ a_n \ | \ e^{\lambda_n \sigma_1}, \quad \lambda_n = \lambda_{N(\sigma_1)}$$
$$\mu \ (\sigma_2) = | \ a_m \ | \ e^{\lambda_m \sigma_2}, \quad \lambda_m = \lambda_{N(\sigma_2)}$$

since

$$\sigma_2 > \sigma_1, \ \lambda_m > \lambda_n,$$

hence

$$\mu(\sigma_2) = |a_m| e^{\lambda_m \sigma_2} = \left(\frac{e^{\sigma_2}}{e^{\sigma_1}}\right)^{\lambda_m} |a_m| e^{\lambda_m \sigma_1}$$

$$\leqslant \left(\frac{e^{\sigma_2}}{e^{\sigma_1}}\right)^{\lambda_m} \mu(\sigma_1),$$

also

$$\mu(\sigma_2) \geqslant |a_n| e^{\lambda_n \sigma_2} = |a_n| e^{\lambda_n \sigma_1} \left(\frac{e^{\sigma_2}}{e^{\sigma_1}}\right)^{\lambda_n}$$

$$= \mu(\sigma_1) \left(\frac{e^{\sigma_2}}{e^{\sigma_1}}\right)^{\lambda_n},$$

these two inequalities taken together give the result.

Alternatively.—Since

$$\log \mu(\sigma) = \log \mu(\sigma_1) + \int_{\sigma_1}^{\sigma} \lambda_{N(t)} \, dt$$

$$\log \mu(\sigma_2) \leqslant \log \mu(\sigma_1) + \lambda_{N(\sigma_2)} (\sigma_2 - \sigma_1)$$

$$\geqslant \log \mu(\sigma_1) + \lambda_{N(\sigma_1)} (\sigma_2 - \sigma_1)$$

hence the result follows.

Corollary.—If 'a' is a constant $(0 < a < 1)$ then

$$\lim_{\sigma \to \infty} \frac{\mu(\sigma a)}{\mu(\sigma)} = 0. \tag{3.2}$$

From 3.1 we have putting $\sigma_1 = a\sigma$ and $\sigma_2 = \sigma$

$$[e^{-(1-a)\sigma}]^{\lambda_{N(a\sigma)}} \geqslant \frac{\mu(a\sigma)}{\mu(\sigma)} \geqslant [e^{-(1-a)\sigma}]^{\lambda_{N(\sigma)}}. \tag{3.3}$$

As $\sigma - \infty$, $\lambda_{N(\sigma)}$ and $\lambda_{N(\sigma a)} \to \infty$, the extremes in (3.3) tend to zero. Hence 3.2 follows.

4. There is still another set of results that can be deduced from the relation

$$\log \mu(\sigma) = \log \mu(\sigma_0) + \int_{\sigma_0}^{\sigma} \lambda_{N(t)} \, dt.$$

Let us set

$$V(\sigma) = e^{\rho\sigma}$$

$$\lim_{\sigma \to \infty} \sup. \inf. \frac{\log M(\sigma)}{V(\sigma)} = \frac{T}{t}, \tag{4.1}$$

$$\lim_{\sigma \to \infty} \sup. \inf. \frac{\lambda_{N(\sigma)}}{V(\sigma)} = \frac{\gamma}{\delta}. \tag{4.2}$$

THEOREM 5.—If $f(s)$ is an entire function of order ρ, then

$$\gamma \geqslant T\rho \geqslant t\rho \geqslant \delta.$$ (4.3)

Proof.—Let $0 < \delta < \infty$, then for $k \geqslant 0$ we have

$$\log M\left(\sigma + \frac{k}{\rho}\right) \geqslant \log \mu\left(\sigma + \frac{k}{\rho}\right) = A_1 + \int_{\sigma_0}^{\sigma + k/\rho} \lambda_{N(t)}\, dt,$$

by 4.2

$$\frac{\lambda_{N(\sigma)}}{V(\sigma)} > \delta - \epsilon \quad \text{for} \quad \sigma > \sigma_0, \ \epsilon > 0,$$

hence

$$\log M\left(\sigma + \frac{k}{\rho}\right) \geqslant A_2 + \frac{\delta - \epsilon}{\rho} e^{\rho\sigma} + \lambda_{N(\sigma)} \frac{k}{\rho},$$

so that

$$Te^k \geqslant \frac{\delta}{\rho} + \frac{\gamma k}{\rho}, \quad te^k \geqslant \frac{\delta + \delta k}{\rho}.$$

If we take $k = 0$, we get $t \geqslant \dfrac{\delta}{\rho}$.

Further from (4.2) we have

$$\frac{\lambda_{N(\sigma)}}{V_{(\sigma)}} < \gamma + \epsilon \quad \text{for} \quad \sigma > \sigma_0, \ \epsilon > 0,$$

hence

$$\log M(\sigma) \sim \log \mu(\sigma) = A_3 + \int_{\sigma_0}^{\sigma} \lambda_{N(t)}\, dt + \frac{\gamma + \epsilon}{\rho} V(\sigma),$$

or

$$T \leqslant \frac{\gamma}{\rho},$$

therefore

$$\gamma \geqslant \rho T \geqslant \rho t \geqslant \delta,$$

or

$$\liminf_{\sigma \to \infty} \frac{\lambda_{N(\sigma)}}{V(\sigma)} \leqslant \liminf_{\sigma \to \infty} \frac{\log M(\sigma)}{V(\sigma)} \leqslant \limsup_{\sigma \to \infty} \frac{\lambda_{N(\sigma)}}{V(\sigma)},$$

provided $0 < \rho < \infty$ **and** $\log M(\sigma) \sim \log \mu(\sigma)$.

3

Theorem 6.—If $f(s)$ is an entire Dirichlet series of order ρ, $0 < \rho < \infty$, then

$$\delta \leqslant \frac{\gamma}{e} e^{\delta/\gamma} \leqslant \rho T \leqslant \gamma, \tag{4.4}$$

and

$$\delta \leqslant \rho t \leqslant \delta \left(1 + \log \frac{\gamma}{\delta}\right) \leqslant \gamma. \tag{4.5}$$

From these two relations it follows that if

$$\lambda_{N(\sigma)} \sim \gamma V(\sigma),$$

then

$$\log M(\sigma) \sim \frac{\gamma}{\rho} V(\sigma).$$

We shall show that

$$\gamma \leqslant e\rho T \quad \text{and} \quad \delta\left(1 + \log \frac{\gamma}{\delta}\right) \geqslant \rho t$$

are the best possible results.

Proof.—We have

$$\log M\left(\sigma + \frac{k}{\rho}\right) \sim \log \mu\left(\sigma + \frac{k}{\rho}\right) = k_1 + \left(\int_{\sigma_0}^{\sigma} + \int_{\sigma}^{\sigma + k/\rho}\right) \lambda_{N(t)}\, dt,$$

hence

$$e^k \frac{\log M\left(\sigma + \frac{k}{\rho}\right)}{\exp.\left[\rho\left(\sigma + \frac{k}{\rho}\right)\right]} > 0 \left(e^{-\rho\sigma}\right) + \left(\frac{\delta - \epsilon}{\rho}\right) + \frac{\lambda_{N(\sigma)}}{e^{\rho\sigma}} \cdot \frac{k}{\rho}$$

or

$$e^k t \geqslant \frac{\delta + \delta k}{\rho}, \quad e^k T \geqslant \frac{\delta + \gamma k}{\rho},$$

taking $k = 0$ in the first inequality and $k = (1 - \delta/\gamma)$ in the second, we have

$$t \geqslant \frac{\delta}{\rho}, \quad e\rho T \geqslant \gamma e^{\delta/\gamma} \geqslant e\delta$$

since for

$$X \geqslant 0, \frac{\exp.(X)}{X} \geqslant e.$$

Further

$$\log M \left(\sigma + \frac{k}{\rho} \right) \leqslant k_3 + (\gamma + \epsilon) \frac{V(\sigma)}{\rho} + \lambda_{N(\sigma+k/\rho)} \cdot \frac{k}{\rho},$$

hence

$$e^k T \leqslant \frac{\gamma + k\gamma e^k}{\rho},$$

$$e^k t \leqslant \frac{\gamma + \delta k e^k}{\rho},$$

taking $k = 0$ in the first inequality and $k = \log(\gamma/\delta)$ in the second, we get

$$T \leqslant \frac{\gamma}{\rho}$$

and

$$\rho t \leqslant \delta \left(1 + \log \frac{\gamma}{\delta} \right) \leqslant \frac{\gamma}{\delta} \cdot \delta = \gamma.$$

THEOREM 7.—For each positive ρ and positive T, there exist an entire function of order ρ and type T, such that

$$\gamma = \lim_{\sigma \to \infty} \sup. \frac{\lambda_{N(\sigma)}}{V(\sigma)} = \rho e T.$$

Proof.—Let

$$\mu_1 = 1, \quad P = 1 + [\rho], \quad \mu_{n+1} = \exp.(\mu_n{}^P), \quad n = 1, 2, 3 \ldots \ldots$$

and

$$f(s) = \sum_1^\infty \left(\frac{e^s}{\mu_n} \right)^{e\rho\tau\mu_n{}^\rho}$$

which is an entire Dirichlet series of order ρ.
Further

$$\left(\frac{e^\sigma}{\mu_n} \right)^{e\rho\tau\mu_n{}^\rho}$$

is the maximum term, if

$$\phi(n) \leqslant \sigma \leqslant \phi(n+1),$$

where

$$\phi(n) = \frac{1}{\mu_n{}^\rho - \mu_{n-1}{}^\rho} [\mu_n{}^\rho \log \mu_n - \mu_{n-1}{}^\rho \log \mu_{n-1}].$$

Let k be a constant such that the maximum of $(0, \rho - 1) < k < 1$, then for $n > n_0$

$$\log (\mu_n) < \phi (n) < \log (\mu_n + \mu_n{}^k) < \log \mu_n + \frac{1}{\rho}$$

$$< \log \mu_{n+1} < \phi (n + 1)$$

and hence if

$$\phi (n) \leqslant \sigma < \phi (n + 1),$$

we have

$$\frac{\log M (\sigma)}{V (\sigma)} \sim \frac{\log \mu (\sigma)}{V (\sigma)} = \frac{eT \log \left(\dfrac{e^\sigma}{\mu_n}\right)^\rho}{\left(\dfrac{e^\sigma}{\mu_n}\right)^\rho} \leqslant eT \cdot \frac{1}{e},$$

since

$$\frac{\log X}{X} < \frac{1}{e}.$$

Further, if

$$\sigma (n) = \log \mu_n + \frac{1}{\rho}$$

$$\frac{\log M [\sigma (n)]}{\exp. [\rho\sigma (n)]} \sim \frac{e\rho T\mu_n{}^\rho}{e\mu_n{}^\rho} \left[\log \mu_n + \frac{1}{\rho} - \log \mu_n\right] = T.$$

Moreover

$$\frac{\log M (\mu_n)}{\exp. (\rho\mu_n)} \to 0, \quad \text{as } n \text{ tends to infinity,}$$

hence

$$t = 0 \text{ and } \delta = 0.$$

Lastly, if

$$\sigma = \log [\mu_n + \mu_n{}^k],$$

then

$$\frac{\lambda_{N(\sigma)}}{V (\sigma)} = \frac{e\rho T\mu_n{}^\rho}{\exp. [\rho \log (\mu_n + \mu_n{}^k)]} \sim \rho eT,$$

hence

$$V = e\rho T.$$

5. THEOREM 8.—Given ρ $(0 \leqslant \rho < \infty)$ and any increasing function $\psi(X)$, such that

$$\limsup_{X \to \infty} \frac{\log \psi(X)}{X} \leqslant \rho \tag{5.1}$$

then there exist an entire Dirichlet series, such that

$$\liminf_{\sigma \to \infty} \frac{\psi(\sigma) \log M(\sigma)}{\lambda_{N(\sigma)}} = 0 \tag{5.2}$$

and

$$\limsup_{\sigma \to \infty} \frac{\log M(\sigma)}{\sigma \lambda_{N(\sigma)}} = 1 \tag{5.3}$$

Proof.—We may suppose without any loss of generality that

$$\frac{\log \psi(X)}{X} \geqslant 2 \ (X \geqslant 2),$$

since if (5.3) holds for a certain $\psi(X)$ it will hold for every $\psi_1(X)$, such that

$$\limsup_{X \to \infty} \frac{\psi_1(X)}{\psi(X)} < \infty.$$

Hence

$$\frac{\log \psi(X)}{(X)} \quad \text{and} \quad \frac{\log \psi(2X)}{X}$$

tend to ρ as $X \to \infty$. Let

$$\mu_1 = 1 + e^\bullet, \ \mu_{n+1} = \exp. \{\exp. (\mu_n)\}, \ a_n = [\psi(2\mu_n) (\log \mu_n{}^2)]$$

$$n = 1, 2 \ldots.$$

and

$$f(s) = \sum_1^\infty \left(\frac{e^\bullet}{e^{\mu_n}}\right)^{a_n}.$$

We can show that $f(s)$ is an entire Dirichlet series of order ρ. Further for all

$$n > n_0, \ a_n < a_{n+1}.$$

For

$$\sigma = \sigma_n = \mu_n + \log\left[1 + \frac{1}{\psi(2\mu_n) \log \log \mu_n}\right],$$

and

$$\lambda_{N(\sigma)} = a_n$$

$$\frac{\psi(\sigma) \log M(\sigma)}{\lambda_{N(\sigma)}} \sim \frac{\psi(\sigma_n) \lambda_{N(\sigma)}}{\lambda_{N(\sigma)}} (\sigma_n - \mu_n) \sim \frac{\psi(\mu_n)}{\psi(2\mu_n) \log \log \mu_n} \to 0$$

as $n \to \infty$. Further for $\sigma = \mu_{n+1}$

$$\frac{\log M(\sigma)}{\sigma \lambda_{N(\sigma)}} \sim \frac{a_n (\mu_{n+1} - \mu_n)}{a_n \mu_{n+1}} \to 1 \quad \text{as} \quad n \to \infty.$$

Dr. S. M. Shah has obtained similar results for entire functions defined by a power series.[8, 9]

I am thankful to Prof. P. L. Srivastava for his help in the preparation of this note. I am thankful to the Referee for his criticism.

REFERENCES

1. YUNG, Y. C., 1951, *Ann. Scien. l'ecale Norm Sup.*, **68.**

2. VALIRON, G., 1949, *Lectures on Integral Functions.*

3. SUGIMURA, K., 1929, *Math. Zeit. Bd.*, **29.**

4. REHMAN, Q. I., 1956, *Tohoku Jour. of Math.*, **8.**

5. ———, 1956, *Math. Student*, **4.**

6. SHAH, S. M., 1941, *Jour. of Indian Math. Soc. (NS)*, **5.**

7. HARDY, G. H., 1924, *Order of Infinity* (Cambridge).

8. SHAH, S. M., 1948, *Quat. Jour. Math.*, Oxford Ser. (I), **19.**

9. ———, 1950, *Ibid.*, Oxford Ser. (2).

STUDIES IN THE VARIATION OF PHYSICAL PROPERTIES OF HUMIFIED CLAYS AND SOIL

Part VI. Changes in Clay, Silt, Porosity, Sticky Point and Wilting Percentage

BY OM PRAKASH BANSAL AND ABANI K. BHATTACHARYA

(Department of Chemistry, Agra College, Agra)

IN the previous publication (Bansal and Bhattacharya, 1952, 1953) of this series, were communicated the results of the studies of the changes in the pH, conductivity and exchangeable bases of Agra soil and three types of clays during the process of humification in presence of raw organic matter. Although any correlation hardly exists between the clay fraction in clays or soil with pH and conductivity, we communicate in this paper the results of our investigations on the variations of clay percentage and changes in some of physical constants such as porosity, sticky point and wilting percentage. Relation between clay percentage, carbon and total exchangeable bases has also been discussed. Williams (1932) gave an empirical formula correlating the clay fraction with the oxidisable carbon and total exchangeable bases in the soil, given by the formula:

$T = 0 \cdot 57 \, K + 6 \cdot 3 \, C$ where T = toal exchangeable bases, K = clay and C = oxidisable carbon.

The opinion that prevails in general, is that the clay content of soil gives a clue to know its reactivity and also its moisture-holding capacity. The capacity of aeration, swelling, loss on ignition, plasticity and crumb formation are also supposed to be connected with the clay content of a soil.

Coutts (1929) determined the sticky point, clay content and water content of a number of Natal soils. It was observed that there was a correlation between the clay content, loss on ignition, sticky point and pore space. Sreenivasan and Subrahmanyan (1934) observed that manuring of red loam with *Pongamia glabra* leaves causes an increase in the percentage of fine particles in the soil. Tiulin and Biryukora (1933) observed that the structure of podsolic soil is improved by clover sod and other fertilizers. The work of F. H. King (1907) on the percentage of pore space of typical soils has shown that the pore space is increased by addition of organic matter and may rise upto 60% or more in grass soils. Keen and Coutts (1928) placed considerable emphasis on the value of the sticky point, *i.e.*, the moisture content at which the attractive power of the soil for water has been satisfied; and it is generally believed on the basis of a good deal of experimental evidence that highly organic soils show high values of sticky points.

Briggs and Shantz (1912) introduced the concept of another physical constant to express the moisture content of the soil—the wilting point. Bouyoucos (1939) observed that addition of organic matter to light soils markedly increased the wilting percentage.

In the light of the above references, it seems that the humification of clays or soil by raw organic matter has not so far been investigated in relation to the

147

TABLE I

	Cabon %	Clay %	Silt %	Sticky point	Poro-sity	Wilting %	Total exchangeable bases		
							A*	B*	C*
SOIL									
Untreated	·32	13·6	19·8	29·8	45·1	0·676	28·13	8·68	27·89
Humified with cauliflower leaves	·49	9·7	26·6	30·4	54·0	..	..	..	..
Humified with spinach leaves	·22	16·0	20·0	31·1	51·0	..	..	..	..
Humified with murena leaves	·29	10·8	21·1	32·5	45·5	..	..	..	..
Humified with neem leaves	·95	12·7	21·7	35·1	56·1	2·308	29·15	13·01	29·95
Humified with cow dung	1·17	13·9	26·6	70·2	64·3	1·440	33·86	14·80	33·57
KASIMBAZAR CLAY									
Untreated	·068	23·5	52·2	45·6	61·0	0·268	25·85	13·70	25·50
Humified with cauliflower leaves	·18	20·0	56·8	51·8	70·0	..	31·06	12·3	22·31
Humified with spinach leaves	·125	22·0	54·0	49·2	67·6	..	25·00	13·31	24·22
Humified with murena leaves	·138	12·3	65·0	48·5	63·66	..	22·19	7·93	13·86
Humified with neem leaves	·45	18·4	58·6	56·25	..	2·511	23·48	13·6	21·97
Humified with cow dung	2·07	..	..	62·9	74·8	..	26·66	..	..

A* By experiment.
B* By Williams' formula.
C* By the formula $T = K_1$ clay $+ K_2$ carbon.

Calculated values for	K_1 *and*	K_2
Soil ..	1·96	6·0
Kasimbazar clay ..	1·07	5·1

TABLE I (*Contd.*)

	Carbon %	Clay %	Silt %	Sticky point	Poro-sity	Wilting %	Total exchange bases		
							A*	B*	C*
RAJMAHAL CLAY									
Untreated	·068	9·65	76·45	30·0	70·3	0·308	14·06	5·9	5·19
Humified with cauli-flower leaves	·194	39·5	35·7	35·8	54·0	..	27·20	23·63	21·23
Humified with spinach leaves	·135	51·1	28·7	32·4	71·0	..	18·94	29·83	27·28
Humified with murena leaves	·114	28·0	45·4	..	..	..	42·85	..	..
Humified with neem leaves	·639	37·3	43·8	31·2	74·2	2·316	16·19	25·28	20·78
Humified with cow dung	2·152	40·6	32·2	68·8	72·6	..	23·33	35·74	24·64
SIMULTALA CLAY									
Untreated	·053	21·4	58·2	47·24	61·0	0·749	14·06	12·4	16·76
Humified with cauli-flower leaves	·230	19·5	60·5	53·5	71·1	..	23·60	12·55	17·16
Humified with spinach leaves	·182	20·5	54·0	50·1	67·8	..	16·66	12·81	17·31
Humified with murena leaves	·180	14·8	62.3	48·2	62·9	..	16·54	9·56	13·07
Humified with neem leaves	·735	19·2	61·8	54·9	73·8	4·22	22·67	15·57	22·03
Humified with cow dung	1·77	17·2	57·3	67·2	73·9	3·062	24·41	20·90	31·12

A* By experiment.
B* By Williams' formula.
C* By the formula $T = K_1 \text{ clay} + K_2 \text{ carbon}$.

Calculated values for

		K_1	*and*	K_2
Rajmahal clay	..	·53		1·6
Simultala clay	..	·76		10·2

clay percentage and the above physical properties. In view of some evidence found in the literature that there may be some relation of physical constants of soils with the content of raw organic matter, we have carried out investigations on the porosity, sticky point, wilting percentage, clay and silt percentages of three types of clays, *viz.*, Rajmahal, Kasimbazar and Simultala—and also of Agra soil after their humification with different kind of leaves such as neem, spinach, cauliflower and murena and cow dung for four months under laboratory conditions. It may be noted, however, that the stage of humification could not be determined for lack of any precise and suitable criterion to warrant the last stage of the decay of organic matter resulting in the form of humus.

EXPERIMENTAL

The clays and soil were humified as described in our previous publication (Bansal and Bhattacharya, 1953). The samples were taken after 4 months and dried in open air. The dried sample was powdered and sieved (2 mm.)

Determination of porosity.—Percentage of pore space was determined by the method recommended by Knowles and Watkin (1947).

Determination of sticky point.—The sticky point was determined by the method of Piper (1947).

Determination of wilting percentage.—The wilting percentage was determined by the method recommended by Marshall and William (1942). Wheat plant was used for the determination of wilting point.

The clay and silt percentage.—It was determined by pipette method (Piper, 1947).

Total exchangeable bases and oxidizable carbon were determined by the methods of Schofield (1933) and Walkley and Black (1934) respectively.

DISCUSSION

1. Table I shows that leaves in general decrease the percentage of clay and increase the silt percentage.

2. The decrease in percentage of clay took place in Agra soil, Kasimbazar and Simultala clays after humification but Rajmahal clays showed an increase.

The decomposibility of silicates by mineral acids has shown that those containing higher percentage of aluminium and iron are attacked less easily than the alkali and alkaline earth silicates (Ephraim, 1949). It may be expected that the organic acids behave similarly and decompose the silicates containing less of iron and aluminium more easily. It was observed (Bansal and Bhattacharya, 1952) that Rajmahal clay was more reactive to water than Kasimbazar clay. Since clays are hydrolysed during humification, it may be suggested that comparatively more colloidal matter would be formed during the humification of such clays as contain lesser percentage of iron and aluminium. The lower percentage of Ca, Mg (*loc. cit.*) may also help to increase the percentage of colloidal matter. From quantitative analysis (*loc. cit.*) we find that Rajmahal clay has got the least percentage of rion and aluminium and also of Ca and Mg. Hence an increase in the clay content of Rajmahal clay seems to be probable,

3. The raw organics decrease the clay percentage of Simultala, Kasimbazar clays and of Agra soil in the following order:

Murena leaves > neem leaves > cauliflower leaves > cow dung > spinach leaves in majority of cases.

In the case of Rajmahal clay the order of increase by the raw organics is as follows:

Spinach leaves > cow dung > cauliflower leaves > neem leaves > murena leaves. Its reverse behaviour is interesting but the reason for it is not clearly understood.

4. It is clear from the table that in most cases the organic matter tends to increase the porosity, sticky point and the wilting percentage also. The capacity of different organics to increase the sticky point and porosity can be mentioned in the following order both in clays and Agra soils:

Cow dung > neem leaves > cauliflower leaves > spinach leaves > murena leaves in majority of cases.

The exception to this order has been found in a few cases, as for example, in the case of Rajmahal clay, where they are irregularities.

5. The wilting percentage has also been found to increase when the original soil or clays are humified with organic matter.

The percentage of clay in all the samples are not in accordance with the variations of sticky point, porosity as well as of wilting percentage. Considering the mineral constituents of soil and clays we cannot ignore the structural modification which incidentally influence the character and number of pore space and hence the sticky point and also the wilting percentage. The contribution of humus and of the inorganic humus complexes towards the porosity is not adequately known. It can be reasonably suggested that humus, clay and silt fractions, contribute together to the porosity, sticky point and wilting percentage of the clays and soils, so that direct proportionality between the clay alone and the above physical properties may or may not exist. This is what we actually observe (*vide* Table I). We are, therefore, of the opinion that the porosity, sticky point and the wilting percentage cannot be correlated with the clay percentage alone unless we have a means of determining other factors, such as hydration capacity, size and shape of the particles which influence the physical properties; and the proportionate contribution of the clay and humus towards the porosity and allied properties.

It will be observed from Table I that the total exchangeable bases calculated from Williams' formula do not agree with those values experimentally obtained by us for the humified Agra soil and the clays. There is a considerable variance of our experimental values for the exchangeable bases, with those by calculations. The problem now arises why this is so? It is due to the fact that the exchange capacity depends upon the specific character of the soil or of the clay which is influenced not only by the size of the particles and surface of the colloidal complex but also by the structural characteristic of the mineral constituents of the clay particles. In the light of this fact it seems more probable that the constants employed as coefficients in the William's formula must vary with different types of soils or clays to express a fairly correct relation between the total exchangeable bases and the percentages of clay and organic carbon.

Followng this reasoning we have calculated the values of the constants K_1 and K_2 ($T = K_1$ clay $+ K_2$ org. carbon) by taking the average of two or three values of the total exchangeable bases, organic carbon and clay percentage in one set and similarly the average values in the other set of our observations. By solving the simultaneous equations, K_1 and K_2 were obtained. It is interesting to observe that the calculations based on the average experimental values derived from our data agree much better with those values of exchangeable bases actually obtained in most cases.

The relation between the total exchangeable bases, carbon and clay percentages derived by Williams appears to be true, but the constants derived by him cannot be universally applied, and should be calculated individually in order to get a fairly good agreement between the total exchangeable bases, clay and organic carbon by Williams' formula.

SUMMARY

The three types of clays, *viz.*, Rajmahal, Kasimbazar and Simultala and Agra soils were humified with different kinds of leaves and cow dung. On being humified, their clay percentage, sticky point, porosity and wilting percentage have been determined. The effect of different humifiers has been compared with each other. It has been found that the raw organics increase the porosity, sticky point and wilting percentage but no correlation between clay percentage and the above physical properties was observed.

ACKNOWLEDGEMENT

REFERENCES

BANSAL, O. P. AND BHATTACHARYA, A. K., 1952, *J.I.C.S.*, Ind. Ed., 30 and 35.

———————, 1953, *Ind. J. Agric. Sci.*, **23**, 125.

BOUYOUCOS, G. J., 1939, *Soil Sci.*, **47**, 377.

BRIGGS AND SHANTZ, 1912, *U.S.D.A. Bur. Plant Indust.*, 230.

COUTTS, J. R. H., 1929, *J. Agric. Sci.*, **19**, 325–41.

EPHRAIM, F., 1949, *Inorganic Chemistry*, V Edition, 844.

KEEN, B. A. AND COUTTS, J. R. H., 1928, *J. Agric. Sci.*, **18**, 740–65.

KING, F. H., 1907, *Physics of Agriculture.*

KNOWLES, F. AND WATKIN, J. E., 1947, *A Practical Course in Agricultural Chemistry*, 6.

MARSHALL, T. J. AND WILLIAM, R. F., 1942, *J. Agstr. Inst. Agric. Sci.*, **8**, 109.

PIPER, C. S., 1947, *Soil and Plant Analysis.*

SCHOFFIELD, R. K., 1933, *J. Agric. Sci.*, **23**, 252.

SREENIVASAN, A. AND SUBRAHMANYAN, V., 1934, *Curr. Sci.*, **2**, 296.

TIULIN, A. F. AND BIRYUKORA, E. V., 1933, *Chem. Social Agric.*, **2**, 113.

WALKLEY, A. AND BLACK, I. A., 1934, *Soil Sci.*, **37**, 29–38.

WILLIAMS, R., 1932, *J. Agric. Sci.*, **22**, 845,

STUDIES IN CHROMIUM TUNGSTATE SOL

Part I. Surface Tension, Viscosity, Conductivity and Stability of the Sol with the Progress of Dialysis

BY P. C. JAIN AND S. N. BANERJI

(Department of Chemistry, University of Saugar, Sagar)

THE chromium tungstate sol shows all the characteristics of a lyophilic colloid. The surface tension of the sol increases with the decrease in adsorption of colloid material at the interface until it approximates to a static value.

The viscosity measurements show (*a*) an initial decrease followed by (*b*) an exponential increase due to the tendency of aggregation and then (*c*) an abrupt increase which has been explained as due to the formation of ramifying aggregates having loose crystallographic axes. The values of (fraction of the total volume of sol particles to that of whole system) are calculated from the results of viscosity measurements using Einstein's and Guth-Simha's equations and they point to the assumption that the particles are asymmetric, the Brownian movement causing them to fluctuate from their positions producing extra resistance to flow.

General form of the conductance curve of impure sol is dependent upon the nature and the magnitude of the effect produced by the gegenions. At the stages of gelation the changes in conductivity are negligible as the sol attains greater and greater purity.

With dialysis the stability, depending upon the electric charges on the surface of the sol particle, decreases continuously till gel is formed.

INTRODUCTION

While studying the surface tension and the stability of some sols Rossi and Monforte[1] found that their results did not substantiate the hypothesis that with the increase in surface tension the stability of the sol is reduced.

Prakash[2] studied viscosity changes during sol-gel transformation in cases of many sols. Philippoff[3] considered the effect of aggregation on the viscosity of the sol on the basis of hydrodynamic theory and found that where aggregates are asymmetrical, there results increase in viscosity with the increase in the degree of aggregation.

Shapiro and Kolthoff[4] observed that the conductance of AgBr powder is the surface conductance. Mushran and Prakash[5] studied the conductivity and coagulation of positive and negative sols of ferric tungstate.

The viscosity and other properties of some of lyophilic colloids have been studied by Ghosh and Banerji[6] and Banerji and co-workers.[7] They have explained the results from the point of view of aggregation of the particles and subsequent orientation. John Voeks and Tartar[8] found that gegenions influence in the aggregate formation.

Earlier work in the chromium tungastte sol was done by Satya Prakash and Dhar.[9] They prepared gels by adding different quantities of K_2SO_4 to chromium tungstate sol. Afterwards Chakravarti[10] studied the influence of concentration on the viscosity of the sol. Ghosh[11] observed photochemical reaction with this sol as active agent under the influence of light in various stages of polarisation and' found that it showed pronounced dichroism during aggregate formation.

In order to investigate further the characteristics of this sol the surface tension, viscosity, conductivity and stability have been studied at different stages of dialysis.

EXPERIMENTAL

A sol of chromium tungstate was prepared by adding slowly a 30% solution of sodium tungstate to an equal volume of 50% solution of chromium chloride, the excess of the latter acting as peptising agent. The sol thus prepared was kept for dialysis in a parchment bag. Analytical reagents were used for preparation.

The composition of the sol with dialysis is given in terms of percentages of Cr_2O_3, WO_3 and Cl'. Chromium was precipitated as $Cr(OH)_3$, tungsten as tungstic acid and chloride as $AgCl$ and were estimated by the standard methods.[12]

Surface tension measurements were carried out with du Noüy's tensiometer. The observations were taken at $30\cdot0°$ C. under identical conditions, with a precision of $\pm 0\cdot5$ dyne/cm.

Pyrex glass Ostwald's viscometer was used for viscosity measurements. Every time the same volume of the sol was taken to have the same hydrostatic pressure for the flow in the capillary of the viscometer. It was kept in a thermostat maintained at $30°$ C. $\pm 0\cdot1°$ C.

The specific conductivity of the sol was measured at $30°$ C. with the conductivity cell kept in the thermostat as above. Pyrex glass conductivity cell, Doran oscillator and Mullard conductivity bridge were used for the purpose.

At different stages of dialysis stabilities, i.e., coagulation values of the sol were determined with $M/100\ K_2SO_4$ solution. Every time, electrolyte was added quickly and shaken well. The stabilities are expressed in millimoles of electrolyte per liter of the mixture (sol + electrolyte + water).

RESULTS

TABLE I

Composition of the sol with dialysis

Stages of dialysis	Days of dialysis	Percentages of		
		Cr_2O_3	WO_3	Cl'
I	2	2·926	6·180	2·010
II	12	1·370	3·455	0·290
III	24	1·055	2·630	0·088
IV	28	0·975	2·507	0·043
V	30	0·934	2·505	0·009
VI*	31	0·931	2·500	0·003
VII		FORMED GEL		

The sol at different stages of dialysis is marked as I, II, III, IV, V, VI and VII,

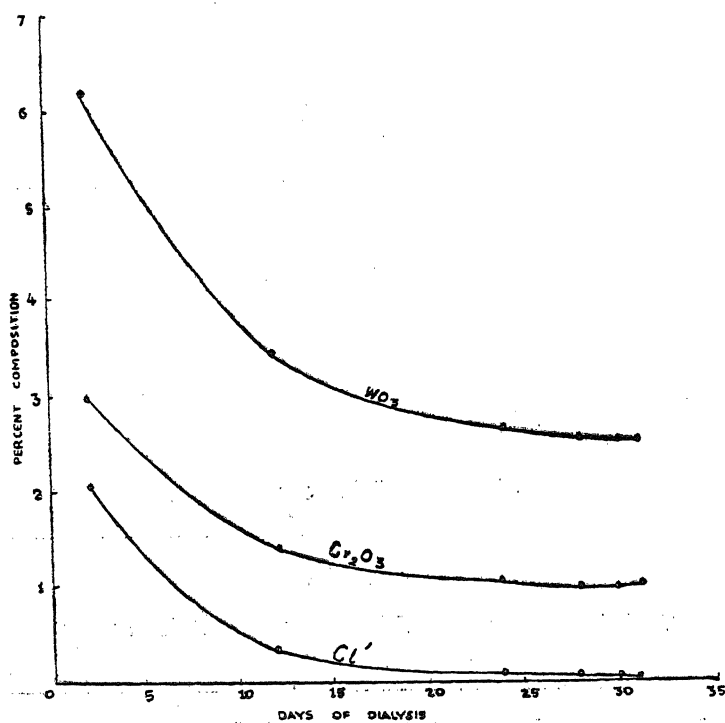The variation in the composition of the sol with the progress of dialysis is shown in Fig. 1.

FIG. 1. Showing the composition of the sol with the progress of dialysis.

TABLE II

. *Surface tension, viscosity and specific conductivity of the sol*
Temperature 30° C.

	Surface tension dynes/cm.	Viscosity centipoises	Sp. conductivity mhos $\times$ 10^{-3}
Water ..	72·1	0·8007	..
Stages of dialysis	Sol	Sol	Sol
I	62·5	1·0630	34·512
II	59·4	0·9141	5·879
III	68·8	0·9636	1·880
IV	69·2	1·2620	0·7379
V	69·8	2·3990	0·5236
VI	70·2	11·2900	0·3617
VII		FORMED GEL	

TABLE III (A)

Stabilities and coagulation values with M/100 K_2SO_4 solution

Volume of sol taken = 2·0 c.c.   Total volume = 5 c.c.

Stages of dialysis	K_2SO_4 in c.c.	Observations after mixing		Stabilities
I	3·0	No coagulation		..
II	3·0	Coagulation after 10 hrs.		>6
III	3·0	,,	$\frac{1}{2}$,,	6
IV	1·5	,,	5 mts.	3
V	0·65	,,	,,	1·3
VI*	0·40	Gel at once		0·6

TABLE III (B)

Sol VI* treated with K_2SO_4 solution and KNO_3 solution

Volume of sol taken = 2·0 c.c.   Total volume = 5·0 c.c.

K_2SO_4 M/100	Observations	KNO_3 M/5	Observations
0·4 c.c.	Gel at once	1·2 c.c.	Gel at once
0·3 c.c.	Gel after 5 mts.	1·0 c.c.	Gel after 2 mts.
0·2 c.c.	Gel after 6 hrs.	0·8 c.c.	Gel after 10 mts.

DISCUSSION

Surface tension.—The experimental results recorded in Table II show that the surface tension of the sol in the initial stages is lower than that of water but it increases with dialysis and after a certain stage it approximates to water.

Working on fatty acid sol Walker[13] concluded that the capillary activities depend more on the aggregated molecules. Banerji[14] has expressed the view that there exists an equilibrium:

Simple molecules ⇌ aggregated molecules ⇌ colloid particles.

Gibbs has shown that if the dissolved material is polar in nature, then it is adsorbed to a greater extent, lowering the surface tension remarkably. According

TABLE IV

The values of using Einstein's and Guth-Simha's equations

Stages of dialysis	Einstein's equation	Guth-Simha's equation
I	0·1312	0·0877
II	0·0566	0·0453
III	0·0814	0·0614
IV	0·2306	0·1320
V	0·7991	0·2982
VI	5·2446	0·8801

to Adam,[15] ' the repulsion between similar electric charges present at the surface lowers the surface tension'.

The initial decrease as observed by us (Table II) may be explained from the above point of view. The rise in its value with the progress of dialysis is mainly due to the decrease in the number of charges at the surface. After certain stage it attains static value. Mc. Bain[16] explains this by supposing that there exists a potential barrier to overcome before a solute can take its final place in the surface and produce after a lapse of time, a final adsorption and static surface tension.

Viscosity.—Three stages of viscosity changes with dialysis have been observed: first a decrease, then an exponential increase and finally a sudden increase near the stages of gelation. The initial decrease may be interpreted on the basis of decrease in the effects of charges and the ionic strength of the medium and hence the energy of dissipation. The exponential increase is mainly due to the tendency of aggregation and decrease in electric charges on the surface of sol particles. The latter effect supports the view of Dhar and Ghosh[17]: the greater the viscosity of the sol, the less is the electric charges on the colloid particle. The sudden increase is due to non-Newtonian flow.[18-20] From time to time different explanations have been given for this behaviour: solvation, electroviscous effect, effect of asymmetry and of structural changes.[16] Although all of these are real, the magnitude of the first two is small. A satisfactory theoretical treatment of non-Newtonian flow has been given by Kuhn and Kuhn.[21] They considered a sol as having ellipsoidal particles. In the laminar flow, the particles are in an equilibrium state dependent upon two opposing forces, one arising from the velocity gradient tending to orient the particles in the direction of stream line flow and the other due to Brownian motion tending to produce random orientation. The latter increases the resistance to flow. Further particles linking up to form large loose aggregates with weak crystallographic axes will increase more and more resistance to flow and thus the energy of dissipation causing an abrupt increase of viscosity as in stages V, VI, Table II, Fig. 2.

A

From Table IV it is seen that with dialysis the volume of sol particles, *i.e.*, increases enormously. This is not due to solvation or immobilisation of solvent molecules round the particles but is due to increase in the degree of asymmetric aggregation for which Simha has given a modified equation.[22]
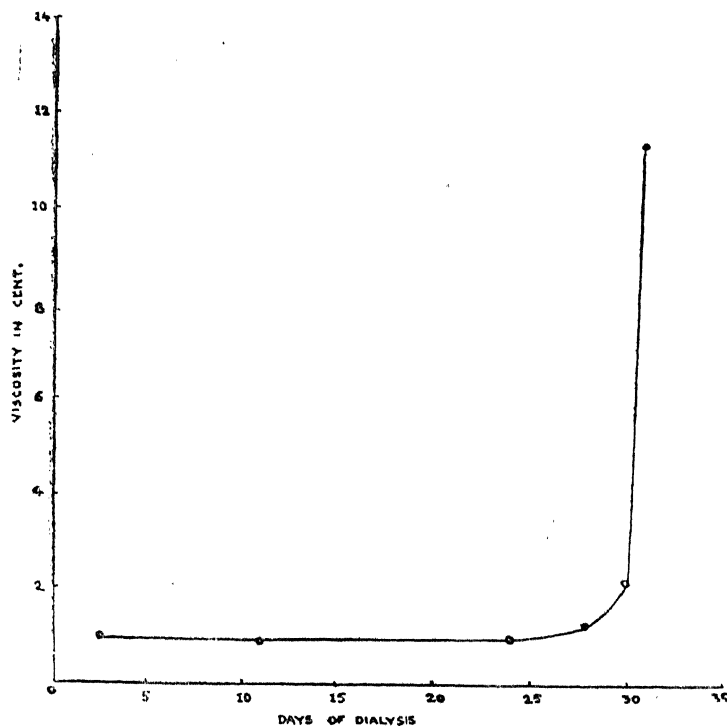

FIG. 2. Showing the changes in viscosity of the sol with the progress of dialysis.

Conductivity.—The specific conductivity at the initial stages is high usually resembling that of an electrolyte because of the presence of chromium, chloride and sodium ions along with sol particles of chromium tungstate. With the progress of dialysis, surrounding electrolyte is removed and aggregation takes place. The latter decreases the effective surface for adsorption. These effects give rapid fall in conductivity, until it reaches an approximate constant value. Slight decrease in the last stages is because of electrophoretic time of relaxation and aggregate formation which decrease ionic mobility and consequently specifiic conductivity to certain extent (Table II, Fig. 3).

With dialysis it is seen that stability decreases (Table III A). For coagulation, the controlling factor is the energy required to bring the two particles together against the action of electric field of the charged particles.[23] According to Hamaker[24] the electrolytes added depress the maxima of potential energy curves till at flocculation value it is too small to prevent coagulation.

In our experiments 0·4 c.c. K_2SO_4 and 1·2 c.c. KNO_3 solutions formed gel at once while lesser amounts than this formed it after some time. This is in accord with Smoluchowski's[25] theory of coagulation according to which coagulation (under suitable condition, gelation) is due to collisions of particles either by

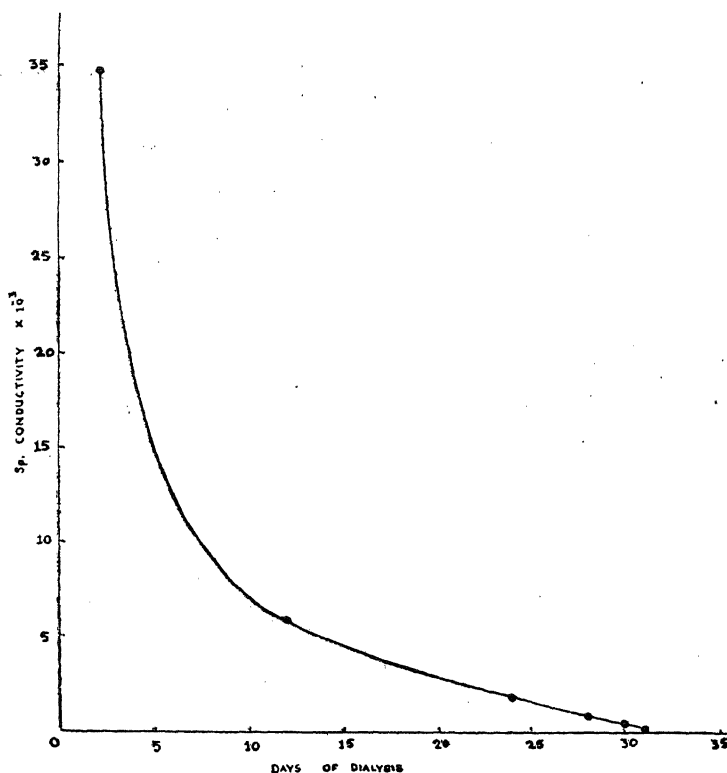Brownian motion or by ceasing off the repulsion between the charged particles with the addition of electrolytes.

FIG. 3. Showing the changes in specific conductivity with the progress of dialysis.

The specific nature of the ions[26] from which colloid particles are formed also play important role in coagulation. Because of this, dilute as well as concentrated solutions of KNO_3 and KCl did not coagulate the sol but formed gel at the greater purity of the sol, *i.e.*, stage VI of dialysis (Table III B).

REFERENCES

1. ROSSI, G. AND MONFORTE, F., 1942, *Chem. Abst.*, **36**, 6394[5].

2. PRAKASH, S., 1952, *Kolloid Z.*, **128**, 15–18; 1951, *Ibid.*, **121**, 147–51.

3. PHILIPPOFF, W., 1944, *Chem. Abst.*, **38**, 3183[4].

4. SHAPIRO, I. AND KOLTHOFF, I. M., 1949, *Ibid.*, **43**, 2071[a].

5. MUSHRAN, S. P. AND PRAKASH, S., 1946, *J. Ind. Chem Soc.*, **23**, 445.

6. BANERJI, S. N. AND GHOSH, S., 1933, *Proc. Nat. Acad. Sci.*, **2**, 135–40; 1939, *Ibid.*, **9**, 148–53.

7. KHER, Y. G. AND BANERJI, S. N., 1952–53, *Saug. Univ. Journal*, **1**, 163–67.

8. VOCK, J. F. AND TARTAR, H. V., 1955, *J. Phys. Chem.*, **59**, 1190–91.

9. PRAKASH, S. AND DHAR, N. R., 1930, *J. Ind. Chem. Soc.*, **7**, 367.

10. CHAKRAVARTI, D. N., 1934, *Proc. Nat. Acad. Sci.*, **21**, 214.

11. GHOSH, J. C., 1937, *J. Ind. Chem. Soc.*, **14**, 518.

12. VOGEL, I., 1951, *Quantitative Inorganic Analysis*, 453, **574**–75.

13. WALKER, 1921, *J. Chem. Soc.*, **119**, 1521.

14. BANERJI, S. N., 1952, *J. Ind. Chem. Soc.*, **29**, 273.

15. ADAM, 1941, *Physics and Chemistry of Surfaces*, 336.

16. MC. BAIN, J. W., 1950, *Colloid Science*, 54–58, 114..

17. DHAR, N. R. AND GHOSH, S., 1928, *Proc. Ind. Sci. Cong.*, **15**, 273.

18. ALEXANDER, A. E. AND JOHNSON, P., 1951, *Colloid Science*, **2**, 595.

19. EINSTEIN, A., 1908, *Z. Electro. Chem.*, **14**, 235.

20. GUTH, E. AND SIMHA, R., 1936, *Kolloid Z.*, **74**, 266.

21. KUHN, W. AND KUHN, H., 1946, *Chem. Abst.*, **40**, 789[5]; 1948, *J. Chem. Phys.*, **16**, 838; 1955, *Ibid.*, **23**, 1526.

22. SIMHA, R. J., 1940, *J. Phys. Chem.*, **44**, 25.

23. EILERS, H. AND KORFF, J., 1940, *Brit. Chem. Abst.*, **111 A**.

24. KRUYT, H. R., 1951, *Colloid Science*, **1**, 87; HAMAKER, H. C., 1936, *Rec. Trav. Chim.*, 1015; 1937, **3**, 727.

25. SMOLUCHOWSKI, V., 1916, *Z. Phys.*, **17**, 556–57, 585.

26. BOZO TEZAK, E. J., 1955, *J. Phys. Chem.*, **59**, 771.

STUDIES ON THE MINERALOGY OF SOME INDIAN CERAMIC CLAYS

By Amal Kumar Bhattacharya, Miss Kamala Zutshi
and Abani Kumar Bhattacharya

(*Department of Chemistry, Agra College, Agra*)

Abstract

Four typical Indian ceramic clays—Rajmahal, Kasimbazar, Katni and Chitrakoot—have been analysed quantitatively. The cation exchange capacity, conductivity, SiO_2/R_2O_3 ratio, swelling and shrinkage of the clays have been determined and critically discussed with a view to suggest the types of clay minerals present in the clay complex. Evidences have been obtained from these determinations that these ceramic clays are mainly mixtures of Kaolinite and other types of more complicated structures containing Calcium, Magnesium, Sodium and Potassium.

Introduction

The clay minerals have been broadly classified into seven main groups, the most common of them being Kaolinite, Montmorillonite and Illite. Among these minerals, the structure of Halloysite was studied in great detail by X-ray diffraction by Mehmel,[1] Edelman and Favejee,[2] Stout,[3] and Hendricks.[4] The structure of Montmorillonite was studied by Maegdefrau and Hofmann,[5] Marshall,[6] and Hendricks[7]. The Illite minerals were studied elaborately by Mauguin.[8] Jackson and West[9] and Hendricks and Jefferson.[10] Brindlay and Robinson,[11] studied the complicated structure of Chlorite minerals.

Chemical analysis of such ceramic clays have shown that they contain variable percentage of Si, Al, Fe, Ca, Mg, Na and K in their composition. Quantitative analysis of four different types of Indian ceramic clays—Rajmahal, Kasimbazar, Katni and Chitrakoot—obtained from the Government Pottery Works, Khurja (U.P.), has been performed. The cation exchange capacity, conductivity, SiO_2/R_2O_3 ratio, swelling and shrinkage of the clays have also been determined and an attempt has been made to discuss the clay mineralogy in the light of their chemical composition and the foregoing physical properties.

Experimental

Silica was estimated by the standard method[12] by fusing with sodium carbonate and treating the insoluble silica with HF. To estimate Rutile, the residual SiO_2 ignited mass after treating with HF was again fused with Na_2CO_3 treated with HCl and filtered. The insoluble matter remaining as residue was Rutile. The above was filtrate mixed with the bulk filtrate for Fe, Al, Ca and Mg, obtained from the previous fusion treatment. Fe, Al, Ca and Mg were estimated in the bulk filtrate by the standard methods. Titanium was estimated as TiO_2 from amongst the metals of the third group by igniting the cupferron compound, $Ti(C_6H_5O_2N_2)_4$.

Conductivity was measured in the clay suspension which was prepared by mixing 100 mesh-sieved clay with water in the ratio 1 : 5.[13] The suspension was thoroughly shaken by a mechanical shaker. The specific conductance was then determined for each sample by Kohlrausch Bridge (PYE) at constant temperature.

In order to observe the swelling properties the clay suspensions which were obtained by mixing 100 mesh-sieved clay with water in the ratio 1 : 5 were filtered through a graduated cylindrical vessel fitted at the bottom with a filtering pad. The volume of the moist clay column after draining out the water gave qualitatively the measure of swelling in each case for the same quantity of the dried clay taken. On drying the moist clay under identical conditions, it was possible to compare their shrinkage. The same experiments were repeated on the flat surface of a Buckner funnel and it was observed that the shrinkage could be compared by observing the size and number of cracks on drying the clays. This was, of course, a qualitative study for the sake of comparison.

OBSERVATIONS

TABLE I

		Rajmahal	Kasimbazar	Katni	Chitrakoot
SiO_2	..	27·160	25·340	29·590	23·960
Fe_2O_3	..	3·500	6·630	5·224	4·604
Al_2O_3	..	46·280	58·420	55·890	62·570
TiO_2	..	..	..	3·749	..
Rutile	..	..	..	3·773	2·580
CaO	..	3·750	1·820	1·305	0·412
MgO	..	1·540	0·250	0·187	0·107
Na_2O	..	0·210	1·954	2·167	1·497
K_2O	..	1·030	1·754	1·796	2·433
Moisture and other radicals, unaccounted for	..	16·530	3·832	..	1·836
SiO_2/R_2O_3	..	0·95	0·67	0·85	0·62
Total Cat. Ex. Capacity	..	15·5	48·4	15·5	47·5

DISCUSSION

Reference to Table I will indicate that SiO_2, Fe_2O_3, CaO, Na_2O, Al_2O_3 are present in variable amounts in Rajmahal, Kasimbazar, Katni and Chitrakoot clays. The proportions of Al_2O_3 and SiO_2 vary more widely than others.

TABLE II

Conductivity, shrinkage and swelling of the ceramic clays

Clays	Sp. conductance	Order of swelling	Order of shrinkage
1. Rajmahal	$1\cdot9 \times 10^{-3}$ Mhos	Chitrakoot > Rajmahal > Kasimbazar > Katni	Chitrakoot > Rajmahal > Kasimbazar > Katni
2. Kasimbazar	$1\cdot66 \times 10^{-3}$,,		
3. Katni	$7\cdot26 \times 10^{-4}$,,		
4. Chitrakoot	$2\cdot19 \times 10^{-3}$,,		

A study of the SiO_2/R_2O_3 ratio of the clays may give some indication of the degree of weathering and hydration of the parent clay minerals. This ratio may further suggest the degree of reactivity of clays and may probably throw some light on the age of weathering and also of the geological strata which might have favoured the process of leaching. The values of the SiO_2/R_2O_3 of Rajmahal, Kasimbazar, Katni and Chitrakoot clays (Table I) are low and found to vary between 0·95 (Rajmahal) to 0·62 (Chitrakoot). The loss of silicon, according to the prevailing view, may be due to (1) the effect of temperature in the tropics which speeds up chemical and biological reactions and (2) the process of leaching to which silicon is more susceptible than aluminium or iron.[14] Grim[15] has further suggested that one type of clay mineral may gradually change into another by weathering, *e.g.*, Kaolinite may weather into a residue of aluminium or iron oxides with loss of silicon. The changes in the composition of Rajmahal, Kasimbazar, Katni and Chitrakoot clays lend enough support to the view mentioned above. The ratio of SiO_2/R_2O_3 should, however, be discussed with caution, since the value of this ratio in any sample of clay depends not only upon the nature of the clay minerals, but also upon the impurities in the estimated SiO_2.

But we observe a low value of the ratio (·95 to ·62) in the ceramic clays; hence the role of temperature and leaching of SiO_2 under tropical heat or change of one clay mineral into another seems to be possible, in spite of the fact that some impurity of SiO_2 may remain associated with the clay.

In Table I it will be seen that Rajmahal and Katni clays have almost identical cation exchange capacity (15·5 m. eq.), while Kasimbazar and Chitrakoot clays have much higher values (47–48 m.eq.). Since cation exchange is due to the broken bonds around the edges of the silica-alumina units or due to substitutions within the lattice structure of trivalent aluminium or quadrivalent silicon and also by the replacement of the hydrogen of the exposed OH groups by a cation, it may be suggested on the basis of the cation exchange capacities that Rajmahal and Katni clays have similar silica-alumina units. On the same basis Kasimbazar and Chitrakoot clays can be visualised to be composed of similar silica-alumina units.

The data on the conductivity of ceramic clays, given in Table II, show that Chitrakoot and Rajmahal clay suspensions are much more conducting than Kasimbazar and Katni clays. Conductivity gives us a measure of the soluble

electrolytes liberated from the clay minerals. Hence it may be suggested that the hydrolytic reactivity of Chitrakoot and Rajmahal clay is greater than Kasimbazar and Katni clays.

It is extremely interesting to note that the swelling and shrinkage of these clays are in the same order as their conductivities. It, therefore, follows that swelling and shrinkage are apparently connected with the quantities of the soluble salts. This can be understood from the fact that a clay which is chemically more reactive is likely to be hydrated to a much greater degree with the result that swelling becomes more pronounced. When the clay is dried, the soluble salts crystallise and hence the binding strength of the particles is lost, and in consequence of this shrinkage becomes visible.

The above investigations on the chemical composition, exchange capacity, conductivity, swelling and shrinkage are of much significance to assess the merits of these clays in ceramic industry. The refractoriness and fusibility should depend mainly upon the composition and structure of the clay lattice, but the presence of soluble salts and the exchangeable cations may also influence these properties. The plasticity is connected with the hydration of the complex and swelling with the expansion of the lattice by the penetration of water molecules. It can, therefore, be suggested, a priori, that by investigating the physical properties in these lines it may be possible to standardise the quality of the Indian ceramic clays.

REFERENCES

1. MEHMEL, 1935, Z. Krist., 90, 35.

2. EDELMAN AND FAVEJEE, 1940, Ibid., 120, 417.

3. STOUT, 1939, Soil Sci. Am. Proc., 4, 177.

4. HENDRICKS, 1938, Am. Mineral, 23, 851.

5. MAEGDEFRAU AND HOFMANN, 1937, Z. Krist., 98, 299.

6. MARSHALL, 1935, Ibid., 91, 433.

7. HENDRICKS, 1942, J. Geol., 50, 276.

8. MAUGUIN, 1927, Compt. rend., 185, 288.

9. JACKSON AND WEST, 1930, Z. Krist., 76, 211; 1933, Ibid., 85, 160.

10. HENDRICKS AND JEFFERSON, 1939, Am. Mineral, 24, 729.

11. BRINDLAY AND ROBINSON, 1951, Mineralogical Soc. of Great Britain, Monograph, Chap. IV, pp. 172–98.

12. SCOTT, Standard Method of Silicate Analysis, 1.

13. PIPER, 1947, Soil and Plant Analysis.

14. THOMSON, 1952, Soils and Soil Fertility, McGraw-Hill, New York, 99.

15. GRIM, R. E., 1942, J. Geol., 50, 225.

CHEMICAL EXAMINATION OF THE SEEDS OF MATTHIOLA INCANA (YELLOW VARIETY)

Part II. Studies on Mucilage

BY D. S. BHAKUNI AND B. C. JOSHI

(Chemistry Department, University of Allahabad, Allahabad)

THE chemical examination of yellow variety of the seeds of *Matthiola incana* R.Br. H.F.B.I. (Hindi *Pili—Towdri*) N. O. *Cruciferæ* revealed the presence of an oil, mucilage, a mixture of colouring matters and an essential oil. The studies on the oil have earlier been described in Part I (Chemical Examination of the Seeds of *Matthiola incana*; Part I—Studies on Oil I).[1]

The freshly extracted pure mucilage was dirty white in colour and fibrous in nature. On complete incineration the mucilage gave 4·5% of greyish white ash which on analysis was found to contain magnesium (1·4%) and iron (1·9%). The hydrolysis of the mucilage with 3% oxalic acid indicated the presence of xylose, arabinose and aldobionic acid. The total percentage of reducing sugars was 16·2%. After being hydrolysed with 3% oxalic acid, the mucilage was hydrolysed with 2-N sulphuric acid when the presence of xylose, arabinose, galactose and galacturonic acid were detected. The total percentage of reducing sugars in the hydrolysate was 24·3%. The mucilage, left after being hydrolysed with oxalic and 2-N sulphuric acids, was hydrolysed with concentrated sulphuric acid when only glucose was obtained. The percentage of the reducing sugars was 20·4%. This indicated that cellulose was present in the mucilage.

EXPERIMENTAL

Extraction of the mucilage.—Six hundred grams of the dried powdered seeds were exhaustively extracted with petroleum ether (40–60° C.) and acetone to remove oil, colouring matters and other organic impurities. The seeds were then soaked in distilled water (600 c.c.) and glacial acetic acid (30 c.c.) was added to the mixture. The contents were then stirred vigorously with a mechanical stirrer for 24–26 hours and filtered through a muslin cloth and the filtrate was added to rectified spirit when a stringy mass was obtained. This mass was then separated by centrifugal method (Yield: 76·8 gm.; 12·8%).

Purification.—The crude mucilage was first dissolved in hot distilled water, acidified with acetic acid (5 c.c. of acetic acid in 100 c.c. of distilled water) and was then filtered. The filtrate was added to the absolute alcohol and the mixture was stirred with mechanical stirrer vigorously when the mucilage was precipitated out. It was taken out and dried. The dried mucilage was successively refluxed with petroleum ether, ether, benzene, chloroform and alcohol to remove all other organic substances which might be contaminated with it. Finally the pure mucilage was dried in vacuum.

The ultimate analysis of the pure mucilage gave:

$$C = 39\cdot7\%; \quad H = 8\cdot12\%.$$

Equivalent weight.—The equivalent weight of the pure mucilage was determined by refluxing for half an hour a known amount of mucilage with a known volume of N/10 caustic potash solution. The excess of alkali was treated against a standard solution of N/10 hydrochloric acid and the equivalent weight was calculated out. It was found to be 1180 approximately.

Ash.—A weighed amount of mucilage was completely incinerated when 4·5% of a greyish white ash was obtained. On qualitative analysis of the ash, only iron and magnesium were found. The quantitative estimation of the ash gave iron = 1·9% and magnesium = 1·4%.

Properties of the mucilage.—The mucilage was insoluble in all the organic solvents. The solubility of the mucilage in distilled water was very low (refractive index of the solution was found to be 1·3328 while that of the distilled water was 1·3336). The viscosity of the gelatinous solution of the mucilage was 1·86 (pH = 2·7) and 2·94 (pH = 5·7) at 20·5° C. and 20 mm. pressure. The viscosity was highest with a pH 6–7·5. On aging the solution, the viscosity decreased rapidly.

HYDROLYSIS OF THE MUCILAGE

With oxalic acid

40·0 gm. of mucilage was taken in a pyrex beaker with 100 c.c. of distilled water and 3 gm. of oxalic acid. The mixture was heated on a water-bath for 24–26 hours. The test portions taken out from the reaction mixture at intervals showed that the hydrolysis started after a lapse of seven and half hours. The hydrolysis took 24–26 hrs. for completion. The solution was filtered and the residue was washed.

The filtrate and the washings were neutralised with $BaCO_3$ and the solution was filtered and concentrated under reduced pressure. The syrup was shaken with methyl alcohol and filtered. The filtrate was tested for sugars and residues for acids.

Sugars.—From the methanol solution, methanol was distilled off and the residue was taken in water and the solution was made upto 100 c.c. The quantitative determination of the sugars indicated that 16·2% of reducing sugars was present in the solution.

The solution was examined chromatographically when the spots of xylose and arabinose were obtained.

The osazones of the sugars were prepared and crystallised with alcohol when two osazones of m.p. 163° C. and 166° C. corresponding to phenylosazones of xylose and arabinose were obtained.

Acids.—Barium in the barium salt of the sugar acid was estimated quantitatively, the percentage of which corresponded to the percentage of barium of the corresponding salt of aldobionic acid.

Found: Ba = 16·25%; Calculated value for Ba of the barium salt of the aldobionic acid = 16·18%.

Confirmation.—The barium salt was oxidised by concentrated nitric acid. The oxidation product was found to be mucic acid (m.p. 210–11° C.).

With 2-N sulphuric acid

The insoluble part of the mucilage left after the separation of the water-soluble products of oxalic acid hydrolysis was further hydrolysed by 2-N H_2SO_4. The product of hydrolysis began to reduce Fehling's solution after a lapse of 5–6 hours and took 26–27 hours for complete hydrolysis. As in oxalic hydrolysis the products of hydrolysis after filtration were separated into sugars and acid-portions. The mucilage left was kept for the hydrolysis with concentrated H_2SO_4.

Sugars.—The sugar solution made upto 100 c.c. was quantitatively estimated and 24·3% of reducing sugar was found to be present in the solution.

The chromatographic examination of the sugar solution indicated the presence of galactose, arabinose and xylose. The presence of these sugars was confirmed by preparing their osazone derivatives when three phenylosazones of these sugars were obtained.

Acids.—Barium of the barium salt of the acid was quantitatively estimated when the percentage of barium corresponded to the percentage of the barium salt of galacturonic acid.

Found: Ba = 25·9%.

With concentrated sulphuric acid

The residue of the mucilage left after the separation of the water-soluble products of 3% oxalic and 2-N sulphuric acids hydrolysis, was finally hydrolysed with concentrated H_2SO_4. The separation of the products of hydrolysis after filtration and subsequent neutralisation of filtrate with $BaCO_3$ showed the presence of glucose only. The presence of glucose was determined by chromatographic examination and confirmed by preparing its osazone derivative. The total percentage of the glucose was found to be 20·4%.

REFERENCE

1. BHAKUNI, D. S. AND JOSHI, B. C.—PART I (forthcoming issue).

ROLE OF GREEN MANURING IN RECLAMATION
PART I

By C. L. Dhawan, B. B. L. Bhatnagar and P. D. Ghai

(*Irrigation and Power Research Institute, Punjab, Amritsar*)

Green manuring is a very old farm practice. It increases the air *cum* water permeability of soil and improves its structure and nutrient status. It has been practised from early times as a means of supplementing animal manure.

Rao and Ghosh[8] reported that the yield of rice, wheat, cotton and sugarcane increased from 13–100% by using San-hemp, Dhaincha, Cowpea, Phaseolus and Cowgram as green manures. Golu-Bev's[4] results indicated the rapid decomposition of green manuring under irrigation and its action could be extended by ploughing it in the autumn to a depth of at least 20–30 cm.

In semi-arid and arid zones, the problem of gradual salinisation and alkalisation of the soils merits immediate attention. Dhawan and his collaborators[3] have carried out intensive work on the reclamation of alkali soils.

Apart from the utility of the other reclaiming agents, *i.e.*, distillery waste, molasses *cum* calcium sulphate, calcium chloride, they have recommended Jantar (*Sesbania aculeata*).

In view of the great possibilities of green manuring for the reclamation of alkali soils, an attempt was made to study in detail the role of different types of green manures for the reclamation of alkali soils.

EXPERIMENTAL

The following green manures were selected for this study:

S. No.	Local Name	International Name
1	Jantar	*Sesbania aculeata*
2	Guara	*Gyamopsis psoralioides.*
3	San	*Crotalaria juncea*

Jantar is an ideal green manuring crop. It can withstand severe draught and will grow on purely drained and slightly saline soils. The crop hardly requires any irrigation, if the germination has once started. Rege and Patwardhan[10] were of the view that Jantar had the additional advantage of reducing salts and improving the structure of the soil. Basu's[2] results showed that with Jantar there was a reduction in exchangeable sodium in alkaline soils.

Guara (*Gyamopsis psoralioides*) is a hardy *kharif* crop, grown mainly for fodder purposes. It is also used as a green manure. In that case it should be sown early and should be ploughed in the land in July and August.

Mukerjee[6] and Sethi and Khan[11] have been investigating the use of San (*Crotalaria juncea* in fixing nitrogen equilibrium of soils.

The following studies were undertaken:

(*i*) Behaviour of the juices in respect of their acidity value with age.

The degree of acidity may be stated in terms of hydrogen-ion concentration.

(*ii*) Determination of total acidity of the juices extracted from the green manuring plants by titrating them with sodium hydroxide and with a sodium soil.

(*iii*) Carbon-nitrogen ratio of the green manures.

(*iv*) Chemical analysis of the juices.

DISCUSSION OF RESULTS

(*i*) *Behaviour of the juices in respect of their acidity values with age.*—The juices were extracted from the green manuring plants and were kept in stoppered pyrex bottles. The variation of temperature during the whole experiment was as follows:

$$\text{Maximum temperature} \quad .. \quad 102° \text{ F.}$$
$$\text{Minimum temperature} \quad .. \quad 36° \text{ F.}$$

The pH values of the juices were determined with a Beckman pH meter at different intervals of time in order to see how far the different chemical reactions taking place in the juices affected their acidity.

Figure 1 shows the variation in pH observed daily for 135 days of Jantar, Guara and San matured after 45 days.
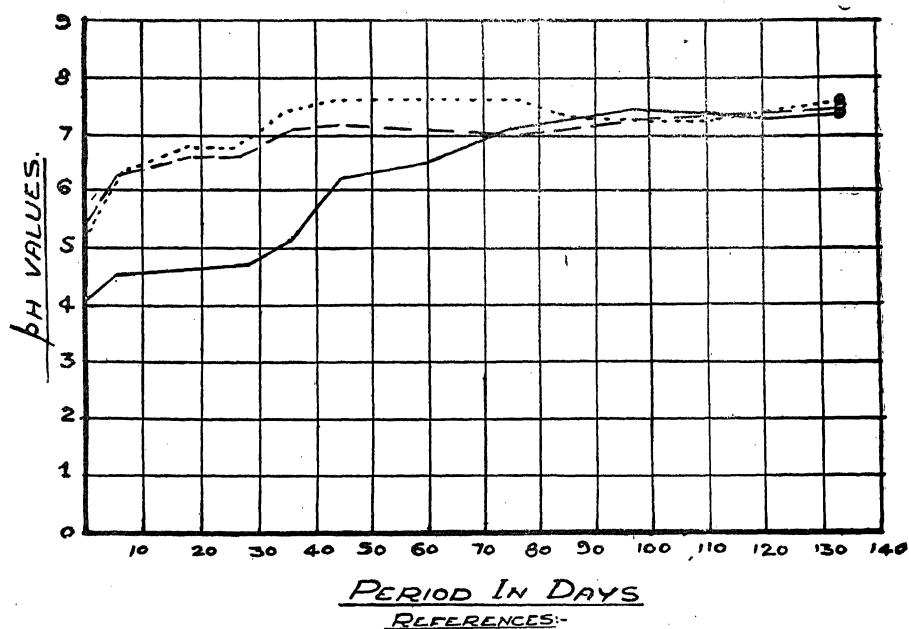
FIG. 1. Showing the variation in pH of the extracts taken from different types of green manures.

Period of maturity = 45 days,

It does not need much emphasis to know that Jantar (*Sesbania aculeata*) has got the maximum acidity as compared with the other two varieties (Fig. 1), *i.e.*, Guara and San.

But our problem is to assess how far can we recommend the use of green manuring for the reclamation of alkali soils.

Alkali soils are characterised by a sodium saturated exchange complex. The sodium saturated colloidal material hydrolyses to form sodium hydroxide and sodium carbonate. Such a system is highly dispersed, highly hydrated and impervious to water. The question, therefore, is to determine the feasibility of the use of green manuring crop for the amelioration of such types of soils.

The pH of Jantar remains below 7·0 for about 70 days (Fig. 1). Therefore the burying of Jantar would naturally bring down the high alkalinity and help in the availability of calcium, usually present in the form of calcium carbonate in semi-arid and arid zone soils for the replacement of sodium in the exchange complex, as about 70·0 mill-equivalents of calcium are soluble at pH 7·0.[9]

The total base exchange capacity of the majority of the soils in the Punjab and Uttar Pradesh varies from 10–20·0 milli-equivalents per 100 gm. of soil. Therefore only one per cent. of calcium carbonate is needed for the replacement of even 20·0 milli-equivalents of sodium in a soil. This much quantity may be present in the alkali soils.

The question naturally arises " what is the comparative acidity of the different parts of the green manuring plants ? "

(ii) (a) *Determination of the amount of sodium hydroxide required to raise the pH of* 10 *c.c. juice extracted from the different green manures to* 7·0.—The juice extracts were titrated with standard sodium hydroxide (N/10) with the Beckman pH meter.

Table I gives the comparative values of N/10 sodium hydroxide required to raise the pH to 7·0.

TABLE I

Sodium hydroxide required to raise the pH of juices to 7·0

(Volume of Juice taken 10 c.c.)

S. No.	Description of the juice		N/10 sodium hydroxide required to raise the pH to 7·0
1	Jantar (stem)	..	65·50 c.c.
2	Jantar (leaves)	..	73·00 c.c.
3	Jantar (whole plant)	..	71·80 c.c.
4	Guara (stem)	..	51·50 c.c.
5	Guara (leaves)	..	61·00 c.c.
6	Guara (whole plant)	..	58·00 c.c.
7	San (whole plant)	..	42·55 c.c.

The following conclusions were drawn from the above study:

(1) The leaves contained the maximum acidity as compared with the stem or the whole plant.

(2) Jantar possessed the greatest acidity. These results supported the views of Joshi.[5]

(*ii*) (*b*) *Titration with sodium soil.*—A sodium saturated soil was prepared from a desaturated soil by the addition of sodium hydroxide. Its pH was 10·2. Increasing amounts of Jantar, Guara and San Juices were added to 10·0 gm. of the soils and the pH of the soil suspensions were determined. The results are given in Table II.

It was confirmed from the results of the titration of the juices with the sodium soil (pH 10·2) that Jantar juice had got the maximum reclaiming power in reducing the pH of the soil (Table II).

With the reduction in pH of the soil, calcium carbonate present in the soil would immediately replace the sodium from the exchange complex.

(*iii*) *Carbon nitrogen ratio of the different parts of the green manures having varying maturity periods.*—This experiment related to the determination of the carbon-nitrogen ratio of the different parts of Jantar, Guara and San.

Carbon was determined by Puri's[7] method and nitrogen by Kjeldahl as modified by Bal.[1]

It is more or less universally accepted that the carbon-nitrogen ratio is one of the most important limiting factors governing the nature and course of the decomposition of plant materials in the soil. Therefore this study was conducted to investigate the comparative behaviour of the green manuring plants at their different ages of maturity in order to judge accurately their fertilizing value.

· The results of moisture, carbon and nitrogen of the different parts of Jantar, Gaura and San with their respective ages are given in Table III.

A glance at Table III brings out the following broad conclusions:

(1) San contains the minimum percentage of nitrogen.

(2) Guara possesses the maximum percentage of nitrogen.

(3) Jantar is midway between Guara and San.

(4) The percentage of carbon increases gradually with age and there is also a little decrease in the percentage of nitrogen.

(5) The range of C/N ratio varies between 8·105–31·54.

Waksmann and Tenny[12] believed that for neutral and alkaline type of soils in temperate regions, a carbon to nitrogen ratio of less than about 22 to 1 is needed for the production of nitrification. It is well known that with the increase in C/N ratio the nitrogen equilibrium of the soil is bound to be affected adversely. Therefore it is very essential that we should preferably not allow the green manuring crops to have maturity period in excess of 4–5 weeks.

TABLE II

Comparison of the reclaiming power of the green manures (Jantar, Guara and San)

(Total volume of the soil suspension—50·0 c.c.)

S. No.	Amount of juice added in c.c.	24 hours			3 days			1 week			3 weeks			8 weeks		
		J	G	S	J	G	S	J	G	S	J	G	S	J	G	S
1	0·0		10·20			10·25			10·20			10·20			10·10	
2	0·5 c.c.	8·80	9·50	9·75	8·35	9·40	9·60	8·00	8·70	8·90	7·25	8·10	7·40	7·35	8·00	8·10
3	1·0 c.c.	7·70	8·60	9·00	7·60	8·50	8·90	7·25	8·20	8·60	6·95	7·80	8·10	7·20	7·50	7·70
4	2·5 c.c.	7·30	8·00	8·40	7·25	8·00	8·35	7·15	7·80	8·00	6·90	7·20	7·65	7·10	7·20	7·50
5	5·0 c.c.	7·00	7·35	8·00	6·95	7·25	7·80	6·85	7·15	7·55	6·85	7·15	7·40	7·05	7·25	7·45
6	7·5 c.c.	6·90	7·10	7·25	6·85	6·95	7·15	6·75	6·95	7·10	6·75	6·85	7·10	6·85	7·00	7·25
7	10·0 c.c.	6·70	7·00	7·10	6·65	6·90	7·05	6·50	6·80	6·90	6·15	6·50	6·70	6·30	6·70	6·90

J. Jantar; G, Guara; S. San

TABLE III

Moisture, carbon and nitrogen values of green manuring plants at different ages of maturity

S. No.	Name of green manuring plant	Age (weeks)	Moisture %	On oven dry basis		C/N ratio
				Nitrogen %	Carbon %	
1	2	3	4	5	6	7
1	Guara whole ..	4	88·90	3·656	41·95	11·47
2	Jantar whole ..	4	90·80	3·758	45·20	12·03
3	San whole ..	4	86·50	3·368	44·51	13·22
4	Guara leaves ..	4	85·42	5·042	41·95	8·32
5	Jantar leaves ..	4	91·15	5·016	44·68	8·91
6	San leaves ..	4	82·13	4·870	41·95	8·61
7	Guara stem ..	4	90·50	1·910	45·10	23·61
8	Jantar stem ..	4	91·20	1·900	48·30	25·42
9	San stem ..	4	84·98	1·710	47·05	27·51
10	Guara whole ..	5	86·40	3·565	43·46	12·19
11	Jantar whole ..	5	86·30	3·175	44·80	14·11
12	San whole ..	5	85·15	2·802	46·21	16·49
13	Guara leaves ..	5	83·51	5·315	43·35	8·15
14	Jantar leaves ..	5	83·35	5·281	46·08	8·72
15	San leaves ..	5	79·53	4·612	43·42	9·41
16	Guara stem ..	5	86·48	2·274	46·62	20·51
17	Jantar stem ..	5	85·16	2·221	47·21	21·25
18	San stem ..	5	81·48	1·868	46·92	25·12
19	Guara whole ..	6	83·82	3·326	48·12	14·47
20	Jantar whole ..	6	83·95	3·176	47·42	14·93

TABLE III—*Contd.*

S. No.	Name of green manuring plant	Age (weeks)	Moisture %	On oven dry basis		C/N ratio
				Nitrogen %	Carbon %	
1	2	3	4	5	6	7
21	San whole ..	6	88·70	2·691	49·68	18·46
22	Guara leaves ..	6	80·70	5·202	44·77	8·61
23	Jantar leaves ..	6	81·26	5·180	49·21	9·50
24	San leaves ..	6	76·79	4·681	44·86	9·58
25	Guara stem ..	6	82·40	2·082	50·06	24·04
26	Jantar stem ..	6	81·92	2·121	50·67	23·89
27	San stem ..	6	80·41	1·625	51·26	31·54
28	Guara whole ..	7	82·31	2·905	48·84	16·81
29	Jantar whole ..	7	81·46	2·862	48·61	16·99
30	San whole ..	7	81·05	2·591	50·70	19·57
31	Guara leaves ..	7	78·50	4·864	51·16	10·52
32	Jantar leaves ..	7	79·29	4·814	46·36	9·63
33	San leaves ..	7	75·68	4·382	50·82	11·59
34	Guara stem ..	7	81·15	1·916	51·56	26·91
35	Jantar stem ..	7	80·76	1·920	52·10	27·13
36	San stem ..	7	78·94	1·621	52·42	32·33

(*iv*) *Chemical analysis of green manuring plants.*—The .chemical analysis of the green manuring plants was carried out for the different chemical constituents in order to determine the availability of calcium for the replacement of sodium from the exchange complex.

The juices were oven dried, ignited and finally digested with concentrated hydrochloric acid for about twelve hours. The acid extracts were examined for the various chemical constituents.

The results of the chemical analysis are presented in Table IV.

TABLE IV

Chemical analysis of green manuring plants on ash basis

S. No.	Name of green manuring plant	Insoluble matter in the acid %	Calcium oxide %
1	Jantar	30·7	34·2
2	Guara	33·5	28·8
3	San	38·6	18·5

The results showed that all the green manuring plants had sufficient percentage of calcium to be used for the replacement of sodium from the exchange complex. But Jantar contained the maximum percentage of calcium.

The juices being acidic in character, the calcium present in the exchange complex would be easily available for the replacement of sodium from the exchange complex.

SUMMARY

(1) Three green manuring plants, *i.e.*, Jantar, Guara and San were investigated for their comparative ameliorative power for the reclamation of alkali soils.

(2) The pH of Jantar juice remained below 7·0 for 70 days.

(3) The maximum acidity was found in Jantar.

(4) The titration of the juices with an alkali soil of high pH value showed that Jantar was comparatively the best reclaiming agent.

(5) Guara possessed the maximum percentage of nitrogen.

(6) San contained the minimum percentage of nitrogen while Jantar occupied the middle position.

(7) The leaves contained the highest percentage of nitrogen as compared with roots and stem.

(8) The C/N ratio increased with age. This means that the age of the green manuring plants deserve primary consideration for burying them in the soil.

(9) Maximum percentage of calcium was present in Jantar.

(10) From the results of different experiments conducted on the three green manures it was concluded that Jantar was the best reclaiming agent for alkali soils.

REFERENCES

1. BAL, D. V., 1925, *J. Agric. Sci.*, **15**, 454.

2. BASU, J. K., 1937, *Proc. Bd. Agric.,* and *Ani.-Husb.-Ind. Soil and Crop Wing* (2nd Meeting), 28.

3. DHAWAN, C. L., BHATNAGAR, B. B. L., SHARMA, R. N. AND AMRIK SINGH, 1952, *Int. Comm.-Irrg. Drain., Annual Bull.,* p. 25.

4. GOLU-BEV, V. D., 1952, *Sovet. Agron. Noh,* 51–56.

5. JOSHI, N. V., 1922, *Bull. Agric. Res. Inst. Pusa,* 14.

6. MUKERJEE, B. K., 1937, *Proc. Bd. Agric. Ani.-Husb.-Ind., Soil and Crop Wing* (2nd Meeting), 28.

7. PURI, A. N. AND SARUP, A., 1937, *Soil Sci.,* **44**, 323.

8. RAO, W. V. B. S. AND GHOSH, A. B., 1952, *Curr. Sci.,* **18**, 170–73.

9. RUSSEL, E. J., 1952, *Soil Conditions and Plant Growth,* p. 561.

10. REGE, R. D. AND PATWARDHAN, G. K., 1956, *Deptt. of Agric. (Bombay) Leaflet.*

11. SETHI, R. L., KHAN, B. N. AND RAO, A. D., 1938, *Bull. Deptt. Agric., U.P.,* 72.

12. WAKSMANN, S. A. AND TENNY, F. G., 1927, *Soil Sci.,* **24**, 317.

CONTENTS